Development on Multifunctional Usages for Straw and Grass as Biomass Resource

（草本系バイオマスの多面的な資源利用に関する研究）

Warachit PHAYOM

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Development on Multifunctional Usages for Straw and Grass as Biomass Resource

By

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ACCEPTANCE

This dissertation entitled “Development on multifunctional usages for straw and grass as biomass resource” hereto attached, prepared and presented by Warachit PHAYOM in partial fulfillment of the requirements for Doctor of Philosophy is hereby accepted.

Shuji FUJITA

Adviser and Chairman

Guidance Committee

SUMMARY

The increasing dependence on fuel and the urgency to reduce greenhouse emissions mentions in an energy policy, and considers the role of renewable sources as energy. Biomass is looked to be a renewable source to supply larger amounts of useful energy with reduced environmental impacts compared to fossil fuel. To offer an important opportunity for the utilization of biomass, this research was investigated from producing biomass using less fossil fuel until developing usages biomass as bio-energy, and emphasized to rice straw which is an abundant biomass.

The main objectives of this research were development new cultivation method for rice using digested slurry produced from biogas plant instead of using chemical fertilizers, and study the characteristics of rice straw and develop usages for rice straw as bio-fuel. The obtained results are listed below:

To investigate the effects of periodic (PDS) and one-time (1DS) application of digested slurry onto wet rice fields by controlled pot cultivation and actual wet rice field test. Both experiments gave similar results on growth duration and nitrogen (N) utilization efficiency. During the tillering stage, plants by PDS appeared less stem number and SPAD values than by 1DS, but those parameters increased during the initial panicle stage and were higher than 1DS during the ripening stage. PDS exhibited significantly higher levels of N uptake, agronomic efficiency, and fertilizer N recovery efficiency than 1DS.

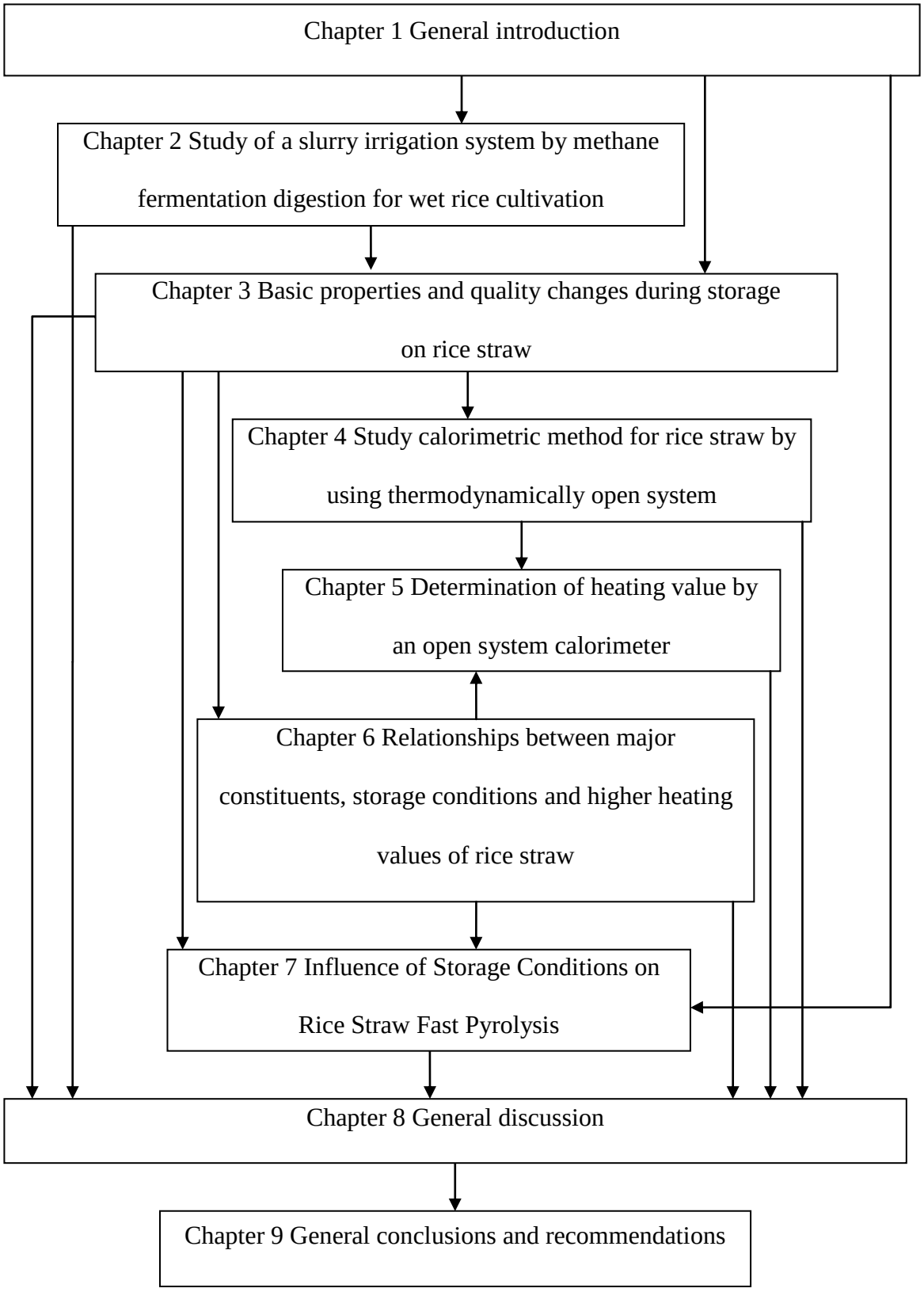
For effects of storage time and temperature on carbon, nitrogen, ash, and moisture of rice straw were studied, storage time and temperature increased, qualities would decrease and rapidly decreased at the first month of storage time and 30°C of storage temperature.

Open system calorimetric (OSC) was developed for estimating heating value. Its uncertainty was ±1.74%, the reported expanded uncertainty was based on a standard uncertainty multiplied by a coverage factor 2 at 95% of confidence level. The relationship between measured heating value by bomb calorimeter and OSC was derived. The heating value model was defined in 3 parameters finally, included combustion output, (E_c), surface output (E_s), and gained heat (E_g), as, HHV = 14.258 + 0.188E_c + 0.026E_s – 0.081E_g in MJ/kg with standard error of estimation ±0.183.

An equation, HHV = 17007.89 – 9.17t + 0.05T, was developed for estimating higher heating value, HHV (kJ/kg) using storage time, t (days) and temperature, T (°C) with coefficient of determination = 0.801 and significance level = 0.05. HHV obtained from this relationship agreed well with those obtained using a bomb calorimeter, indicating that this relationship has the potential for use in estimating HHVs of rice straw.

The finally proposal built up in this research, was to study thermal behavior and indicate influences of storage conditions on the fast pyrolysis of rice straw was studied by TG and DSC. Pyrolysis of rice straw consists of drying, heating, degradation and heating and aggregation of char. Degradation stage was an important stage due to the highest heat flow rate and specific heat occurred. Pyrolysis temperature range would finish around 470°C to 500ºC.

LAYOUT AND FLOW OF DISSERTATION



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NOMENCLATURE, SUBSCRIPTS, AND GREEK SYMBOLS

Nomenclature

1DS	One-time application of digested slurry
A	Ash concentration (%db)
ABE	Average bias error
AE	Agronomic efficiency
A_o	External surface area of open system calorimeter (m)
BC	Bomb calorimeter
C	Carbon content (%)
CF	Chemical fertilizer
C_n	SPAD value on *n* days after transplantation
C_p	Specific heat (kJ/kg°C)
CRD	Completely randomized design
DS	Digested slurry
DSC	Differential scanning calorimetry
E	Energy
E_p	An error term of the predictive model
F	Fixed carbon concentration (%db)
h	Convection coefficient ($W/m^2°C$)
H	Hydrogen concentration (%db)
HHV	Higher heating value
HI	Harvest index
H_n	Plant height on *n* days after transplantation (cm)

I	Current (A)
K	Coverage factor
k	Thermal conductivity (W/mK)
L	Characteristic dimension (m)
LSD	Least significant difference
L_V	Specific latent heat (kJ/kg)
m	Mass (g)
M	Moisture concentration (%)
N	Nitrogen concentration (%db)
N_n	Stem number on n days after transplantation (stem)
O	Oxygen concentration (%db)
ORP	Oxidation – reduction potential
OSC	Open system calorimeter
PDS	Periodic application of digested slurry
PE	Physiological efficiency
r	Correlation coefficient
R	Radius of open system calorimeter (m)
R^2_{adj}	Adjusted coefficient of determination
R^2	Coefficient of determination
RE	Fertilizer N-recovery efficiency
S	Sulfur concentration (%db)
SEE	Standard error of estimate
T	Temperature (°C)
t	Time

TC	Total carbon
TG	Thermogravimetric
t_i	Daily mean air temperature at *i* days after transplantation (°C)
TN	Total nitrogen
u	Uncertainty (%)
U_n	N uptake on *n* days after transplantation (%)
V	Volatile matter (%db)
v	Voltage (v)
X_1	Independent variable (storage period)
X_2	Independent variable (storage temperature)
Y	Dependent variable

Subscripts

1	Outside
2	Inside
a	Air
b	Burned
comb	Remaining material in combustion chamber
cond	Conductive output
conv	Convective output
cw	Condensed water
e	Exit
f	Flue gas
g	Gained heat

I	Entry
inc	Incomplete combustion material
o	Other
p	Electric power
rad	Radiative output
remain	Energy remain in a simple calorimeter
s	Sample
STD	Sapphire standard
surf	Surface
ub	Unburned material
w	Water

Greek symbols

ε	Emissivity of Radiating surface
σ	Stefan Boltzmann constant = 5673 x 10^{-8} W $m^{-2}K^{-4}$
Σ	Sum
Δ	Difference
β_0	Regression coefficient (intercept of this plane)
β_1	Regression coefficient (change in the mean response corresponding to a unit change in X_1 when X_2 is held constant)
β_2	Regression coefficient (change in the mean response corresponding to a unit change in X_2 when X_1 is held constant)

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CHAPTER 1

General Introduction

Recently, soaring world oil price is serious problem because of the rapid worldwide increase of fossil fuel consumption of in the twentieth century. As reports of annual energy consumption statistics by International Energy Agency (2011) in Figure 1.1, it reported historical final consumption data from world coal/peat consumption, world oil consumption, world natural gas consumption, world biofuels and waste consumption (data prior to 1994 for biofuels and waste final consumption have been estimated), world electricity consumption and other (includes geothermal, solar, wind, heat, etc) by fuel. Globally, total energy consumption showed an almost increase from 1971 to 2009. World total consumption by fuel increased from 4,000 to 8,000 Mega tons of oil equivalent (Mtoe, the amount of energy released by burning one ton of crude oil), or by a factor of about 2, accounted as 100 Mtoe of the annual consumption. Klass (1998) expected to the depletion time of the proved reserves of petroleum was 35 years, or the time was depleted on the year 2027. That means the time of using fossil fuel is not too distant. Furthermore, the gradually increasing of carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (N_2O) emissions affect the planet's atmospheric and climate as called greenhouse effect. Fossil fuel consumption was making higher CO_2 emissions in every year. International Energy Agency (2011) reported world CO_2 emissions from 1971 to 2009 by fuel increased from about 14,000 to 28,000 Mt of CO_2 (Fig. 1.2).

It is strongly visible that many countries are attempting to lower or at least maintain atmospheric CO_2 by reducing fossil fuel consumption. As will be shown in next topic, biomass has a very important role in atmospheric CO_2 fluxes. Therefore, new energy

and biomass resources must widely be developed as soon as possible for instead of fossil fuels.

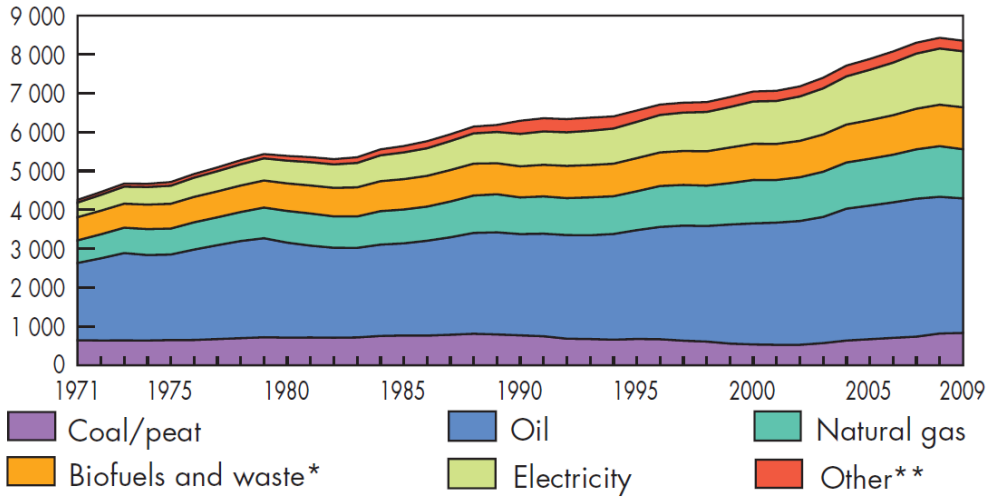


Figure 1.1. World total final consumption from 1971 to 2009 by fuel (Mtoe), International Energy Agency (2011).

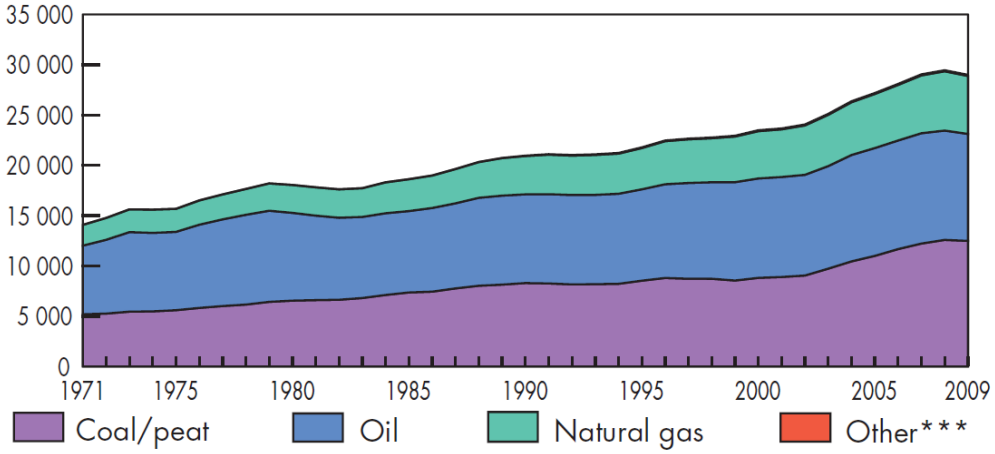


Figure 1.2. World CO_2 emissions from 1971 to 2009 by fuel (Mt of CO_2), International Energy Agency (2011).

1.1 Role of biomass in energy

Alternative fuels are an important topic to a foresight analysis of the world. Biomass is one kind of alternative fuels and a renewable carbon resource for energy, which has the potential of reducing consumption and delayed depletion time of fossil fuels. Carbon or energy in biomass is renewed via a process of photosynthesis with a time span shorter than fossil fuel. By the process, the capture of solar energy or light energy as fixed carbon in biomass through photosynthesis, during which CO_2 is converted to organic compounds, which represented by carbohydrate $(CH_2O)_n$ and 470 kJ (112 kcal) of energy is included in a mole, oxygen (O_2) liberated in the process comes exclusively from the water (H_2O), and is depicted by the equation as follow

$$6CO_2 + 6H_2O \xrightarrow[\text{Light energy}]{} C_6H_{12}O_6 + 6O_2 \quad (1.1)$$

The use of biomass as energy, it can be a zero net CO_2 energy source and does not contribute to increase greenhouse gas emission (The Japan institute of energy, 2008). The basic concept of biomass as a renewable energy resource consists, the capture of solar energy and carbon from ambient CO_2 in growing biomass, which is converted to biofuels, synfuels or is used directly as a source of thermal energy or hydrogen. One cycle is completed when the biomass or derived fuel is combusted. This is equivalent to releasing the captured solar energy and returning the carbon fixed during photosynthesis to the atmosphere as CO_2.

However, the term biomass has very wide meaning and there are many classifications. The Japan institute of energy (2008) categorized to three kinds of biomass resources based on the term of use or application as resources, namely; conventional biomass resources, plantation biomass, and biomass wastes. Table 1.1 shows lists of biomass classification by the Japan institute of energy (2008).

Table 1.1. Lists of biomass classification by the Japan institute of energy (2008)

Supply sector	Type	Example
Conventional biomass resources	Agriculture Forestry (Woody) Fishery Livestock farming Food	Timber Chip Pulp Food waste
Biomass wastes (derivatives)	Agriculture Forestry Fishery Livestock residues	Rice straw Cattle manure Lumber mill Sawdust Sewage sludge
Plantation biomass	Forestry Herbaceous Aquatic	Poplar Oil Palm Corn Sugarcane Giant Kelp Algae

Most biomass used as energy directly is conventional biomass resources and they have been used since long time for domestic heating and cooking, charcoal production, and particle board production generate. In Thailand, chips and bark were produced within various wood processing industries. Most of chip and bark was from rubber trees. It was planted largely in the Southern region. The annual availability of this resource was estimated at 1.84 million tons. Based on a heating value of 10,000 kJ/kg, thus, power

generation potential from wood residues was about 118 MW (National Energy Policy Office, 2000).

Nowadays, plantation biomass is emphasized because of demanding energy. Plantation biomass is planting tree, purely for their use as fuel such as sugarcane, corn, cassava, etc. National Energy Policy Office (2000) reported in Thailand, cassava, the source of tapioca, was a bushy tropical plant producing starch-rich tubers (the underground portion of the plant). Cassava was planted mainly in the Northeast region. Production of cassava roots had averaged about 20 million tons per year. Cassava was processed to make two major products: tapioca pellets and starch/flour. Production of tapioca starch produced waste tapioca skin (peelings) and slurry that could be potential low cost fuels. Total residue availability was 2.5 to 2.8 million tons per year. They had high moisture contents of 67 and 83 percent, respectively. Dry heating values were measured at 15,100 and 15,500 kJ/kg, respectively. In order to utilize cassava residues as fuel, a moisture separation or drying process would be necessary. This would imply additional cost and overall efficiency loss. Based on a reduction in moisture content to 40 percent, it was estimated that heating values would be around 9,150 kJ/kg. Using the residue availability given above, power potential from this resource was estimated at 75 to 84 MW.

However, increasingly, biomass waste is seeing the benefits of using them for power generation such as sawdust, rice husk, etc., this saves disposal costs. In Thailand, there are many kinds of biomass waste. Corncob was one of biomass waste. It was the ear of corn plants which remains after is milled to remove the corn seed. Corn was mostly milled using portable milling machines at locations around the plantations. Thus, most of corncob was left scattered in the field, posing collection difficulty. A small portion was processed in milling shops located in provinces that grow the crop. Based on

milling statistics, corncob constitutes about 25 percent of the corn seed weight. Based on a residue percentage of 25 percent and a collectivity of 50 percent, the annual availability of this resource was estimated at 500,000 tones. Based on a heating value of 15,000 kJ/kg, power generation potential from corncobs was estimated at 54 MW. The corncobs were fed directly into the sugar mill boiler without need for chipping or grinding (National Energy Policy Office, 2000).

Rice field is an important and abundant biomass source in Thailand. It is grown in every region. National Energy Policy Office (2000) reported paddy production over the period from 1986/87 to 1995/96 has averaged about 20 million tones per year. Rice husk is a by-product from rice fields, which is produced during paddy milling. Rice husk constitutes about 23 percent of the paddy weight. If, an annual, there was paddy production of 20 million tones and a residue collectivity of 50 to 80 percent, the availability of this resource was estimated at 2.3 to 3.7 million tons per year. Based on a heating value of 13,500 kJ/kg, power generation potential from rice husk ranged from 234 to 375 MW. Rice husk has been used as fuel for power plants in Thailand.

The one of by-product from rice fields is rice straw. It is agricultural residues and was looked as invaluable in the past. There are multifunctional usages, for examples, animal feed, stall bedding for animals, materials for industrial, soil improver. However, it is still abundant feedstock in fields a year, and because it is evaluated as a potential technically viable feedstock that might be used as low-cost for the production of fuel. Therefore, rice straw is looked as sustainable energy nowadays.

Each year, rice straw is estimated to be 10 Mt-dry a year (Energy for environment foundation, 2006) in Thailand, and 731.3 million tons of rice straw is annually harvested in the world (Keikhosro et al., 2006), and its energy potential is accounted 1191×10^{18} joules as of heating value of rice straw 16.28 MJ/kg (Brown, 2004). It is a well-known

fact that, energy related environmental issues. If all of rice straw were converted to be energy, we could reduce carbon dioxide emissions by reducing usage of coal based electricity (carbon dioxide emission factor of 230 kg/GJ, Klass, 1998) accounted as 2.74×10^9 tones as shown in Table 1.2. However, amount of energy generation depends on conversion factor of each technology.

Table 1.2. Yield, potential energy and reducing carbon dioxide emission from rice straw

Continent	Yield ($\times10^6$ tones)	Energy potential ($\times10^{18}$ J)	Reducing CO_2 emission ($\times10^9$ tones)
Africa	20.9	0.34	0.08
Asia	667.6	10.87	2.50
Europe	3.9	0.06	0.01
America	37.2	0.61	0.14
Oceania	1.7	0.03	0.01
Total	731.3	11.91	2.74

Note: The energy potential = yields × heating value

The reducing CO_2 emission = energy potential × CO_2 emission factor

1.2 General biomass conversion technologies into energy

There are various conversion technologies that can convert biomass resources into a renewable energy source. Conversion technologies may release the energy directly, in the form of heat or electricity, or may convert it to another form, such as liquid biofuel or combustible biogas.

1.2.1 Physical conversion

Physical conversion is process which produce useful energy directly such as firewood and pelletizing. Klass (1998) and The Japan institute of energy (2008) reported, the main procedure of physical conversion consisted dewatering and drying, size reduction, densification, and separation. Dewatering and drying refer to the removal of all or part of the contained moisture from biomass as a liquid and vapor, respectively. Size-reduction techniques are used to prepare biomass into fuel pellets, cubes, and briquettes. Size reduction is often required before biomass is used as a fuel or feedstock. Densification is process to pelletizing consists of feeder, roller, and dies. Separation is process for remove low quality of pellets.

1.2.2 Thermochemical conversion

For thermochemical conversion, this technology is operating under controlled temperature and oxygen conditions to convert biomass into producer gas, liquid, and solid. Thermochemical conversion can decrease bulk of biomass and transfer to the convenient forms as good as energy usage. Thermochemical conversion technology includes combustion, gasification, and pyrolysis:

- Combustion

Klass (1998) defined the combustion technology as, combustion technology included incineration, direct firing, and burning of biomass. The processes consisted of the rapid chemical reaction (oxidation) of biomass and oxygen, the release of energy, and the simultaneous formation of the ultimate oxidation products of organic matter, CO_2 and water. It was also apparent that to achieve maximum flame temperature, dry fuel and small amounts of excess air are required. By use of thermodynamic data, the theoretical temperature at which the products of combustion form under adiabatic, reversible conditions can be calculated.

- Gasification (Klass, 1998; The Japan institute of energy, 2008)

Gasification is typically characterized as incomplete combustion of a fuel to produce a fuel gas of low to medium heating value. Gasification lies between the extremes of combustion and pyrolysis (anaerobic thermal decomposition) and occurs as the amount of oxygen supplied to the burning biomass is decreased. Gasification expands the use of solid biomass to include all the uses of natural gas and petroleum-based fuels, giving it a distinct advantage over combustion. Besides, providing higher efficiency power generation through advanced processes, the fuel gas can be used for the chemical synthesis of methanol, ammonia, and gasoline. The ultimate product is a combustible gas mixture termed as producer gas. This gas has a relatively low calorific value. The typical composition of this gas is carbon monoxide, hydrogen, nitrogen, carbon dioxide, and methane.

- Pyrolysis

For pyrolysis, it is playing important role and attended since the process conditions to produce high energy density pyrolysis liquids in addition to the derived char and gas (Kucuk and Demirbas, 1997). The pyrolysis procedure consist thermal degradation of cellulose proceeds with a gradual degradation, decomposition, and charring on heating at lower temperatures, and a rapid volatilization accompanied on pyrolysis at higher temperatures.

Brown (2004) reported that, the pyrolysis liquid yields were possible to 78% if relative short residence time applied about 0.5 to 2 seconds at 400 to 600°C and rapid quenching. However, the liquid varies from as low as 25 cP up to 1,000 cP, depending on the water content and the original feedstock, black through dark red-brown, with up to 15 to 30% water (BTG Biomass Technology Group BV, 2001). Furthermore, Brown (2004) reported, the liquid was highly oxygenated and a mixture of many compounds, and thus

highly unstable. Due to organic acids which derived from hemicellulosic matters of biomass, thus the pyrolysis liquids were highly corrosive. Range of the higher heating values of the liquids was between 17 – 20 MJ/kg, with density of about 1,280 kg/m^3. Advantages of pyrolysis liquid; it is effectively increasing the energy density of biomass for transportation and storage, and can be the direct application as a substitute for heating oil, fuel for combustion or modified to diesel engines. Therefore pyrolysis liquid is suggested as an integrated approach to production of both chemical and fuel.

1.3 General biomass conversion technologies into fertilizer

The other important technology is biochemical conversion by fermentation (aerobic and anaerobic) which uses micro-organisms in the production of energy (biogas) and fertilizer such as anaerobic fermentation, ethanol fermentation, hydrogen fermentation, etc. Cascade utilization of these materials investigates lower emission for environment and enables more effective usage than mono usage.

Also, biomass can be applied as developed to be fertilizer, due to it contains many essential plant nutrients and organic matter (Carballa et al., 2009, Hou et al., 2007). For converting biomass to fertilizer, composting is the one kind of major treatment methods for solid waste biomass. Methane fermentation is one of anaerobic treatment methods of organic waste that can take methane gas as fuel and digested slurry that can be applied as liquid fertilizer. There were many reports that liquid from anaerobic digestion of livestock wastes contains 90% crude protein and essential minerals (Gnanamani and Kasturi Bai, 1992). Gomez-Gomez and Viniegra-Gonzalez (1977) reported, to use the liquid from anaerobic digestion of animal waste as fertilizer for growing lettuce, there were no significant differences in lettuce production to commercial urea fertilizer, fresh animal waste and a mixture of the partially digested slurry with urea added for growing

lettuce. Besides, there was no detrimental effect on the fertilizer value of the slurry due to its partial digestion, and as methane was also produced and parasite eggs destroyed during this process.

In Asia there are many paddy fields and almost farmers use chemical fertilizers. But their prices are very expensive and there is environmental impact to produce chemical fertilizers by consuming fossil fuel. Instead, liquid fertilizer is inexpensive to produce and less consuming fossil fuel, In Japan, practical application manners of liquid fertilizer may be establishing for paddy agriculture, e.g. how to transport and spread, how to calculate application rate (Iwashita and Iwata, 2010). Digested sludge may be includes many kinds of easily decomposable organic matters that may affect plant growth and soil conditions, which will change to inorganic materials gradually (Hou et al., 2007). But basic knowledge of quality as fertilizer on digested sludge is not clear.

1.4 Thesis objectives, scopes and outlines

Straw and grass are biomass resources and multifunctional usages, for examples, animal feed, stall bedding for animal, material for industrial, soil improver, energy. For decreasing energy and environmental concerns, thus, this study would like to develop straw and grass as biomass resource for energy. There were two main objectives, consist development new cultivation method for rice using digested slurry produced from biogas plant instead of using chemical fertilizers, and study the characteristics of rice straw and develop usages for rice straw as bio-fuel.

In general introduction, this chapter described of role of biomass in renewable resources, especially role of rice straw, and general converting technologies. These approaching conducted to the application of development on multifunctional usages for biomass as renewable resources along the chapters of this thesis.

After the current introductory view, chapter 2 presented the study of the slurry irrigation system by methane fermentation digestion for wet-rice cultivation. It was the one of main contributions of this work. Digested slurry (DS) was interested. DS is a by-product from methane fermentation. Methane fermentation is an effective technology for treatment of livestock manure, sewage sludge, and waste biomass. Methane fermentation converts degradable organic compounds by anaerobic digestion, hydrolysis, acid formation, and methane production (Kaspar and Wuhrmann, 1978) to biogas which is an energy resource, and DS, which is used as a liquid fertilizer for plants (Haga et al., 1979) because of its high ammonium nitrogen (NH_4-N) content, an important nutrient for plant growth (Carballa et al., 2009, Hou et al., 2007). The type of raw material is related to the potential productivity of methane fermentation (Wong et al., 2008). Hou et al. (2007) reported that the total nitrogen (TN) in DS was 3,850 mg/l when the material used was dairy cattle waste, while Furukawa et al. (2009) reported TN of 1,600 – 2,200 mg/l when the material used was a mixture of raw garbage, livestock manure, and sewage sludge. The main characteristics of slurry digested by mesophilic fermentation were 1,400 – 1,600 mg/l of NH_4-N, 1,600 – 2,200 mg/l of TN, pH of 8.5, 2,000 – 3,000 mg/l of suspended solids, 8,000 – 10,000 mg/l of chemical oxygen demand, and 1,000 – 1,500 mg/l of biochemical oxygen demand (Furukawa et al., 2009). This indicates that the constitutes of DS as well as their concentrations must be considered and adjusted to provide optimal conditions for target plants when DS is applied as a fertilizer for cultivation.

DS is used as a liquid fertilizer in various types of farmlands worldwide. European countries and US use DS for grasslands, while Asian countries use it for rice cultivation (Hopkins, 2009, Hou et al., 2007). Many studies have been conducted to compare DS and chemical fertilizer (CF) applications.

Li et al. (2003) reported that no significant differences existed between DS and CFs for plant length, number of tillers, and leaf area indices. However, the same study found that grain and biomass yields of rice with the same N application rate (50 – 70 kgN/ha) and recovery rate (RE) as well as agronomic efficiency (AE) for N from DS were higher than those from CFs, although not significantly. These results corresponded with reports by Liu et al. (2002) and Jeyabal and Kuppuswamy (2001) that grain and straw yields increased on using DS. These results indicate that even when the application volume of DS is decreased, it can still produce the same yields as CF and that the total area of rice fields will be expanded when DS at the same application rate as CF is used. Furthermore, when comparing equal outputs from DS and CF, the environmental load of DS is less than CFs because of the difference in energy consumed during their production.

Therefore, chapter 2 includes comparing the using digested slurry by periodically and one time supplying for wet rice cultivation.

From chapter 3 to chapter 8, emphasized to rice straw as energy. Rice straw was cognized that it is unutilized biomass resources, but these have possibility to be applied for energy as mentioned in the previous part. Rice straw is major product of growing of grain. In Japan, rice grain is produced 9.5 Mt in a year and rice straw is estimated around 9.6 Mt-dry per year (Matsumura et al., 2005). For Thailand, rice straw is estimated to be 10 Mt-dry a year (Energy for environment foundation. 2006). If 19.6 Mt-dry of straw in Japan and Thailand are converted to energy, achieving account for 8,420 million liter of diesel fuel when heating value of rice straw and diesel fuel are 15.2 MJ/kg-dry and 35.4 MJ/L, respectively (Klass, 1998). Rice straw is seasonal, harvested term is limited during autumn season in one year. But processing to energy is a year round activity that means straw is stored long term to use all stocked straw around one year. Moreover, rice straw undergoes strong degradation in a few months after harvest

(Brown, 2004). Therefore, suitable storage conditions to preserve rice straw for periods of a year or even longer are requested.

Therefore, firstly, effects of storage conditions on basic properties of rice straw would be investigated in chapter 3. These data were used for chapters 5 to 7.

Many researchers have studied renewable energy for supporting a critical fuel shortage in the world. To indicate the economic evaluation of material as a fuel, the heating value or calorific value is always investigated because it is one of the most important properties to indicate energy content in material. Due to the heating value is the amount of heat released during the combustion of a specified amount of it (Huang et al., 2008). Many kinds of calorimeter are used to determine heating value of material, especially, the direct determination of energy content from a closed system such as the adiabatic and isothermal calorimeters (Hsi and Kuo, 2008; Sheng and Azevedo, 2005). The principle of calorific measurement of material by adiabatic and isothermal calorimeters is burning material in a controlled boundary and measuring the net temperature rise or the enthalpy change (Sheng and Azevedo, 2005). Also, the closed system apparatuses are the best controlled from some energy which may be gained from or lost to the apparatus, thus, both adiabatic and isothermal calorimeters indicate results with great accuracy. Meanwhile, a closed system apparatus is very expensive.

A calorimeter with mass exchange or open system and with heat exchange or non-adiabatic, is one kind of calorimetric system such as open flame type (Zielenkiewicz, 1989). Open flame system calorimeter can also estimate energy content by temperature rise in the same way as a closed system but by an open system there is a large heat loss to the surroundings and has a low accuracy, but the total cost become low. If it is used such kind of indirect methods as collecting the net heat losses and heat inputs, by using mass and energy balance equations may have the potential for providing calorimetric method

by correcting and estimating by indices from a simple calorimeter.

Therefore, chapters 4 and 5, the other indices from an open system calorimeter (OSC) would be derived to estimate the heating value. Chapter 4 introduced theories of the mass and energy balances to develop a calorimetric method and explains the mathematical procedures for the reliable determination of heating value. Chapter 5 presented the results of the heating value studies that were coupled to the OSC and model. The model was predicted from experimental heating value by bomb calorimeter (data from chapter 6) and by OSC. For measured heating value by OSC, the data from chapter 3 was used as well.

However, using mathematical relationship is another important method obtains the heating value by indirect estimation from proximate and ultimate analyses. From chapter 3, the Food and Agriculture Organization of the United Nations (1994) reported that, storage conditions might be a factor that changes the properties of biomass materials, because biomass materials deteriorate during storage because of biological degradation processes. Therefore, chapter 6 presented the new models for calculating the heating value. The one model was developed from major constituents of rice straw. The other one was derived from storage conditions which conveniently and lowers cost of application for determination of heating value by experiment or elemental analyses are not available.

For energy conversion technologies, there are several technologies to convert rice straw as energy as mentioned in the previous part. Also, thermal conversion process is a technology, including of combustion, pyrolysis, gasification, direct liquefaction, etc. For pyrolysis, it is playing important role to be promising conversion routes of biomass upgrading. This process, feedstock will be converted into liquid (pyrolysis oil), charcoal and non-condensable gases. Pyrolysis has higher fuel yields to feed ratios, higher liquid

with lower yields of unsaturated gas and charcoal than gasification and carbonization. However thermal properties during process are the important keys to adjust the yields of products. Pyrolysis oil can be applied in engines and turbines as heavy oil (The Japan institute of energy, 2008; Bridgwater, 2004; Demirbas, 2001). Chapter 7 exposed the results of thermal behavior of rice straw which was studied by Thermogravimetric (TG) and Differential Scanning Calorimetry (DSC), within the range of slow pyrolysis. Also, the properties from chapter 3 and chapter 6 would be used to explain together with these results.

CHAPTER 2

Study of a Slurry Irrigation System by Methane Fermentation Digestion for Wet Rice Cultivation

2.1 Introduction

Digested slurry (DS) by methane fermentation can be used as a liquid fertilizer of farmlands worldwide as mentioned in the chapter 1. However, if a farmer decides to use DS, a large amount of it has to be transported to the field and applied within a limited time to correspond with plant growth. Therefore, distribution methods of DS to agricultural fields are important. Many techniques are used for the application of DS to crop fields in European countries and US, especially for grasslands (The Asia-Pacific Economic Cooperation: Virtual Center for Environmental Technology Exchange, 2010). The techniques include sprinklers and drip irrigation systems known as "fertigation" (Cassman, 2008, Fangueiro et al., 2008). In Asian countries, especially in Japan, DS is transported as a liquid fertilizer to agricultural fields in vacuum trucks containing several tons of the fertilizer. DS is applied to rice fields by two methods. One is the spray crawler method and the other is the slurry irrigation method, in which DS is mixed with irrigation water, which is then used to irrigate the fields.

In the spray crawler method DS is spread before tilling. During spraying, vacuum trucks bring DS from the facility to the target field and transfer the slurry to the spray crawler. The land is tilled to mix the soil and fertilizer well, and the field is irrigated for rice transplantation (Iwashita and Iwata, 2010) as shown in Figure 2.1. In Japan, a town in Chikujyou developed a spray crawler with a 2.5-ton tank that could spread 5 tons of DS to 1000 m^2 within 18 min with two transshipments from vacuum trucks. Thus, in one

hour, this system can spread 16.5 tons of DS to fields and treat approximately 0.33 ha. However, until the required volume for one rice field is reached, this process would have to be repeated many times because of the limited capacity of the vehicle, and fuel consumption in transportation would be a concern.

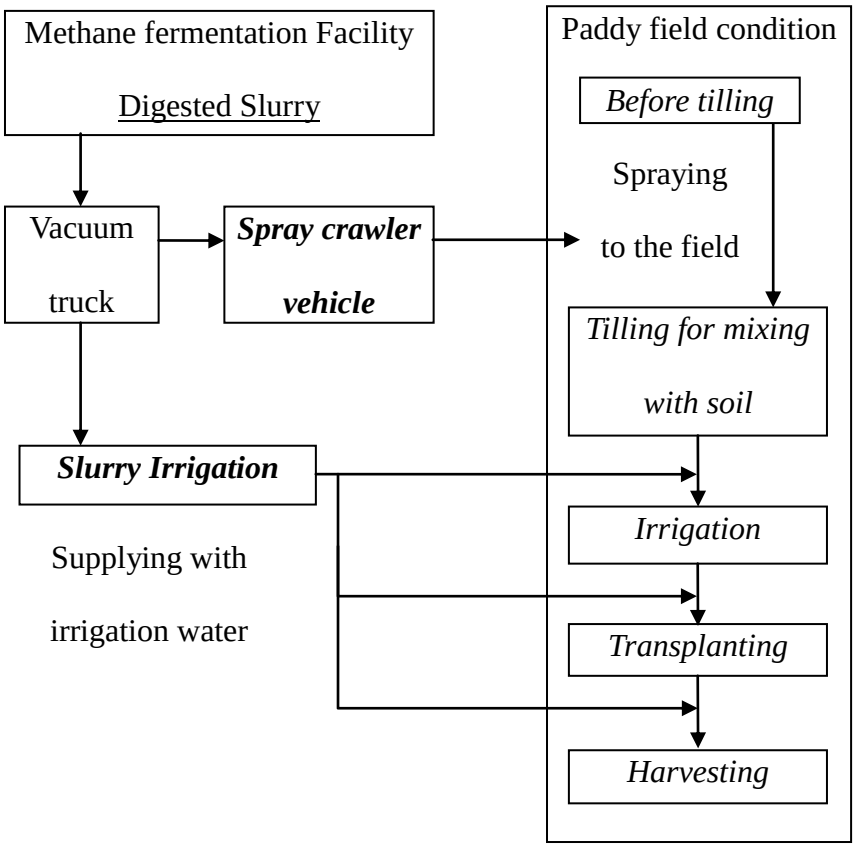


Figure 2.1. Flow charts of methods to supply digested slurry to a field; spraying by crawler vehicle, slurry irrigation method by vacuum truck.

When a mixture of irrigation water and DS is used, vacuum trucks are used to bring and mix the two near the rice fields. This method can be used after irrigation and transplantation as well as during rice growth as a topdressing. In that case, the truck operator should continue to supply a constant volume of DS to water during the entire irrigation time in order to maintain a uniformly mixing of the fertilizer constituents in the

irrigation water for application to the rice field (Iwashita and Iwata, 2010). Consequently, vacuum trucks are occupied during these operations for a longer time period than the spray crawler.

A common limitation to both of these application methods is the long time for completion. Development of a pipeline system to supply DS to fields is assumed to improve this limitation. If pipelines from the facility would directly delivery DS to the rice fields, farmers could control the open system and estimate the volume of DS using a flow meter on a discharge line.

In the case of liquid fertilizers and chemical fertilizer (CF), basal and/or panicle fertilizers are generally applied at one time to the rice field. However, the required periods for fertilizer spreading are approximately the same for farmers cultivating wet rice. In other words, DS usage by farmers is concentrated during the same period. Therefore, a large amount of DS has to be transshipped and distributed over wide areas during a limited time period. Such conditions cause two problems: a difficulty in satisfying all requests from farmers who want to use DS and a decline in the fertilizer utilization ratio caused by the effect of nitrification, denitrification, and runoff from fields. If a farmer decides to use DS at variable intervals and if these intervals become longer than they are at present, then these is a possibility for improvement of these two problems. In addition, Sasahara and Itoh (1989) reported that split application of a fertilizer improved growth conditions for rice and increased yields. The slurry irrigation method may potentially allow frequent or continuous application of DS to a rice field.

To acquire the basic data for the development of a pipeline system, this study focused on differences in the effects of periodic and one-time application of DS (PDS and 1DS, respectively). Main objective was to investigate the effects of continuous application of slurry digested by methane fermentation to a wet rice field as a topdressing with irrigation

water and identify the absorption ability of plants for the fertilizer applied as basal and topdressing, and estimate the amount of biomass yield achieved.

This study was divided into two parts. First, the effects of the application methods of DS on rice cultivation from the viewpoint of growth duration and N use efficiency through controlled pot cultivation tests was studied. Second, rice cultivation tests on actual wet rice fields in Yamaga City to confirm the results of the pot cultivation tests were conducted.

2.2 Materials and methods

2.2.1 DS from methane fermentation

DS in this experiment was obtained from Yamaga Biomass Center in Yamaga City, Kumamoto Prefecture. Raw materials used in the Yamaga Biomass Center are waste biomasses, such as cattle manure, pig manure, and food waste. Compost and methane fermentation are methods to recycle the wastes. Products generated at this center include biogas, DS, and solid fertilizer. Table 2.1 shows amount of raw material are used and products are achieved in Yamaga Biomass Center.

Table 2.1. Amount of raw materials are used and products are achieved in Yamaga Biomass Center

Raw materials		Products	
Cattle manure	63.7 ton/day	Solid fertilizer	4,380 t/year
Pig manure	10.4 ton/day	Liquid fertilizer	17,336 t/year
Food waste	3.0 ton/day	Biomass gas	1,182 m^3/day
Sewage sludge	730 ton/year	Electricity	2,494 kwh/day

2.2.2 Fertilizer concentrations

There were two kinds of fertilizer in this study, DS and chemical fertilizer. For DS, the concentration of components depends on the raw materials added to the methane fermentation tank (Ryu et al., 2010). The concentration of TN, NH_4-N, nitrate (NO_x-N), and total phosphorus (TP) was 1800, 1540, 12, and 26 mg/l, respectively in Controlled pot cultivation tests. For rice cultivation tests at actual wet rice fields in Yamaga City, TN, NH_4-N, NO_x-N, and TP of DS were 2587, 1586, 22, and 827 mg/l, respectively. The amount of nitrogen fertilizer applied was calculated based on the amount of TN and applied as topdressing. For chemical fertilizer, NPK fertilizer (17% of N, 14% of P_2O_5, and 17% K_2O) was applied as basal dressing.

2.2.3 Controlled pot cultivation tests

The objective of this experiment was to investigate the effects of frequency of application of DS to a wet rice field as a topdressing with irrigation water.

The experiment was performed in an experimental greenhouse at Saga University, Japan, from July 9 to October 14, 2009. The area of the greenhouse was 105 m^2 and the roof was covered with transparent plastic sheets. For ventilation and insect screening, the four sides of the greenhouse were covered with window screens and transparent plastic sheets. The rice cultivar used was ‘Morinokumasan’. This is a commended variety bred by Kumamoto Prefecture Agricultural Research Center. The cultivars were transplanted 0.05 m^2 from the soil surface and stood 0.30 m, tall. Wagner pots were made by Kiya Seisakusho, Ltd, and poor sandy soil with 0.1 mgN/kg.

Planting density was three plants in 0.05 m^2 of pot area. Five treatments (A-pot to E-pot) with five replications were arranged in 5 × 5 rows and randomized two times per week (Fig. 2.2). Table 2.2 shows the dates of operations, volume, and varieties of applied fertilizer. A total of 100 kgN/ha of CF was applied as a basal dressing to A-pot

and mixed well and 20 kgN/ha was applied before the panicle stage. Next, 60 kgN/ha of CF was applied as a basal dressing to B-pot through E-pot. Furthermore, 40 kgN/ha (112 g of actual DS applied/pot of actual DS applied) of DS was applied 5 times separately as a topdressing at the tillering stage and 20 kgN/ha (56 g of actual DS applied/pot) was applied at one time as a topdressing before the panicle stage to B-pot. C-pot was supplied with 40 kgN/ha at one time as a topdressing at early tillering stage and 20 kgN/ha one time before the panicle stage. No fertilizer was applied to D-pot after transplantation and E-pot had no plant or fertilizer.

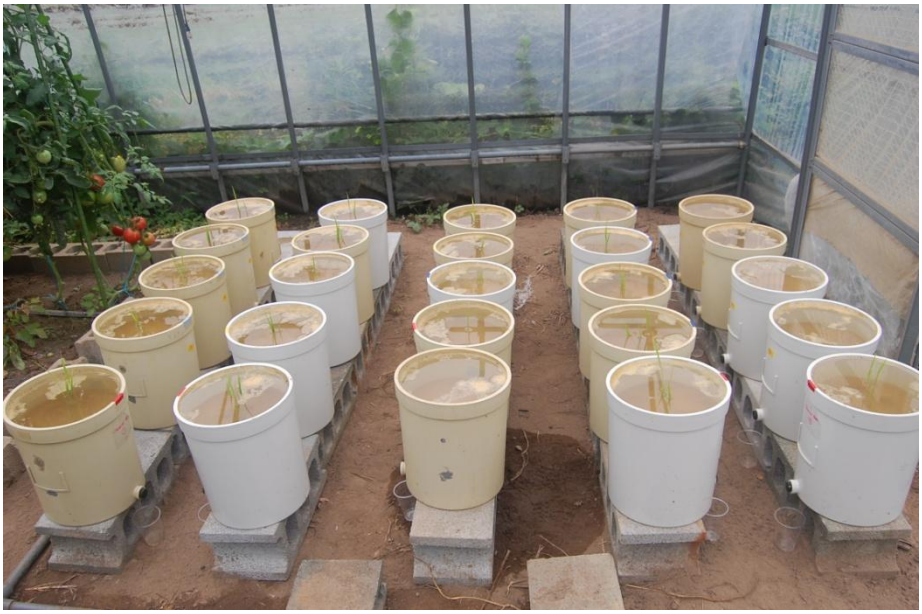


Figure 2.2. Five treatments with five replications in Controlled pot cultivation tests.

Table 2.2. Dates of operations, volume, and varieties of applied fertilizer in controlled pot cultivations tests

Pot experiment	A	B	C	D	E
Planting density, stem/pot	3	3	3	3	-
Basal dressing (Jul 9) - CF, kgN/ha	100	60	60	60	60
Topdressing after transplantation (Jul 10) - DS, kgN/ha (actual DS application, g/pot)	0	40 (23 × 5)	40 (112)	0	0
Topdressing before panicle stage (Aug 18) - CF, kgN/ha - DS, kgN/ha (actual DS application, g/pot)	20 0	0 20 (56)	0 20 (56)	0 0	0 0

Note: A = applied chemical fertilizer, B = periodic application of digested slurry, C = one-time application of digested slurry, D = no applied fertilizer, E = no fertilizer and no plant, DS = digested slurry, and CF = chemical fertilizer.

For every pot during cultivation, the following parameters were measured 2 times per week: the plants height, stem number, and chlorophyll content of leaves as a SPAD unit using a SPAD meter (this instrument was developed by Soil and Plant Analyzer Development by the Ministry of Agriculture, Forestry and Fisheries in Japan). The oxidation status or oxidation–reduction potential (ORP) was measured by an ORP meter. Ambient temperature and solar radiation were also measured. These data were used to estimate N uptake during cultivation by using equation (2.1) (Araki et al., 2005). This

equation was used from 2 to 8 weeks after transplantation, in addition to physiological observation.

$$U_n=11.7+6.57\times10^{-6}\times H_n\times N_n\times C_n\times\sum_{i=0}^{n-1}(t_i-12) \quad (2.1)$$

where, U_n is N uptake on n days after transplantation (DAT), C_n is the SPAD value, H_n is plant height (cm), N_n is the stem number, and t_i is the daily mean air temperature at i DAT.

After harvesting, the rice plants were separated into grain, straw, and root. The weight of each part was measured, and the value was used to calculate the N use efficiency (Delogu et al., 1998, Russell et al., 2006, Jianliang et al., 2008) as follows:

- Gained N uptake (kgN/ha) is the difference in kg of the N content of fertilized and unfertilized treatments
- Harvest index (HI) is the ratio of grain to biomass (kg)
- Physiological efficiency (PE) is the ratio of gained grain to gained N uptake (kg)
- Fertilizer N-recovery efficiency (RE, %) is the ratio of gained N uptake to applied N (kg)
- Agronomic efficiency (AE) is the ratio of gained grain to applied N (kg)

2.2.4 Rice cultivation tests at actual wet rice fields in Yamaga City

This experiment was performed to confirm the results of the controlled pot cultivation tests. The actual cultivation tests were performed in Yamaga City, Kumamoto Prefecture, Japan (Fig. 2.3). Three sections at the tillering stage were used in the experiment: CF, PDS, and 1DS. For PDS and 1DS, DS was applied as a topdressing before the panicle stage. The rice field had a poor sandy loam, and the experimental site included three plots for three treatments. The plot size was 35.6 m in width and 100 m in length for CF treatment and 22.4 m in width and 100 m in length for each DS treatment (Fig. 2.4). The rice cultivar used was ‘Morinokumasan’, which was planted 12.3 hills/m^2. Table

2.3 shows dates of operations, volume, and varieties of applied fertilizer for actual cultivation tests; 53 kgN/ha of CF was applied to the CF plot as a basal dressing and mixed well.

At the PDS plot 130 kgN/ha of DS (11.2 tons of actual DS application/plot area) was applied 5 separate times as a topdressing at the tillering stage and 90 kgN/ha (7.84 tons of actual DS application/plot area) at one time as a topdressing before the panicle stage. At the 1DS plot 130 kgN/ha of DS (11.2 tons of actual DS application/plot area) was applied as a topdressing one time at the early tillering stage and 90 kgN/ha (7.84 tons of actual DS application/plot area) at one time before the panicle stage.

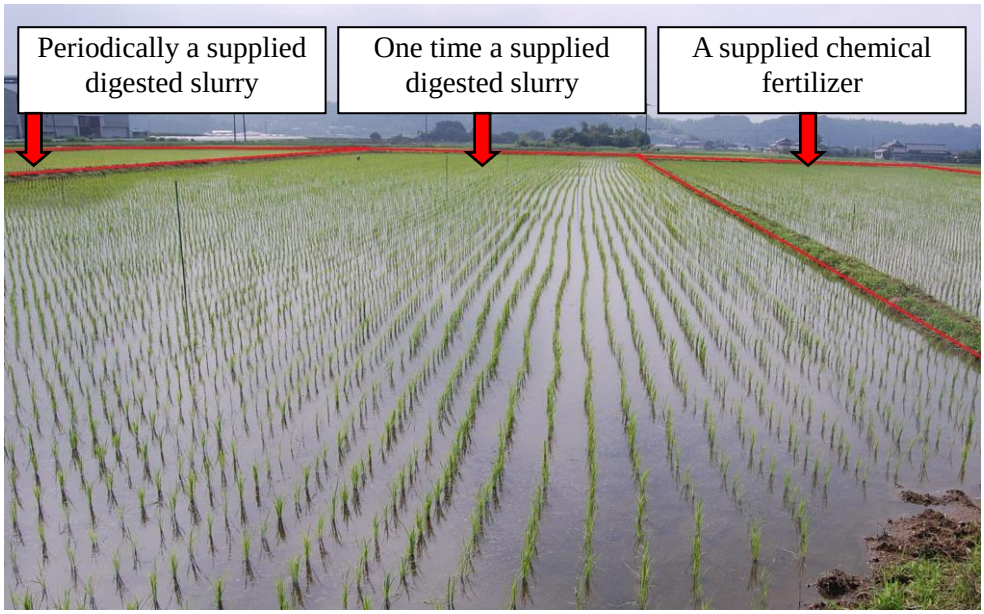


Figure 2.3. The actual cultivation tests in Yamaga City, Kumamoto Prefecture, Japan.

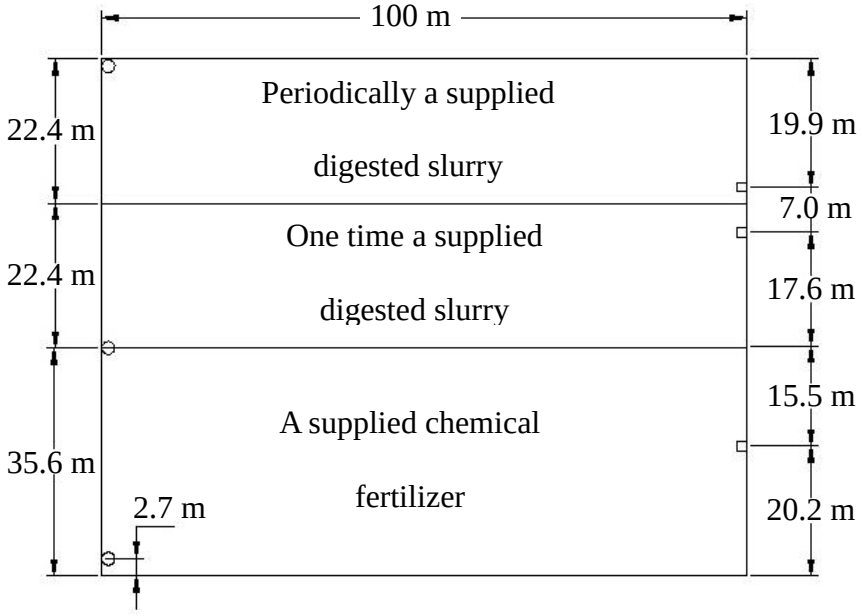


Figure 2.4. Size and positions of water gates (o) and drain (□) of each plot in rice cultivation tests on actual wet paddy fields in Yamaga city.

Table 2.3. Dates of operations, volume, and varieties of applied fertilizer during rice cultivation tests in actual wet rice fields in Yamaga City

Site	CF	PDS	1DS
Area (m^2)	3560	2240	2240
Basal dressing (Jun 21), kgN/ha	53	0	0
Topdressing after transplantation (Jul 1), kgN/ha (actual DS application, t/plot area)	0	130 (2.24 × 5)	130 (11.20)
Topdressing before panicle stage (Aug 18), kgN/ha (actual DS application, t/plot area)	0	90 (7.84)	90 (7.84)

Note: CF = applied chemical fertilizer, PDS = periodic application of digested slurry, 1DS = one-time application of digested slurry, DS = digested slurry.

To control the amount of N in DS, N content was first measured in the laboratory, and the total volume of DS to be applied to the rice field was calculated.

Data analysis was similar to the first part. During cultivation, two monitoring points were set in each plot and 10 plants at one point were measured for the following parameters at every 10 days; a total of 20 plants in one plot were investigated for the plant height, stem number, and chlorophyll content of leaves, measured using a leaf color chart. At maturity, 20 rice plants were taken from each plot to determine the biomass yield and then separated into grain and straw and measured. These data were applied to N uptake calculations and HI.

2.3 Results and discussion

2.3.1 Controlled pot cultivation tests

(1) Growth duration and yield

Table 2.4 shows the dates of stages, differences in air temperatures and solar radiations inside and outside the greenhouse, growth durations, yields, and HIs during the experiment. The temperature difference inside and outside the greenhouse during the experiment was rather large, approximately 3.3°C. The difference in solar radiation inside and outside the greenhouse during the experiment was about 1300 lux.

From the tillering stage (20 DAT), there were no significant differences between the treatments in terms of the stem number, with 12.8, 9.2, 9.6 and 11.2 for A-pot (CF), B-pot (PDS), C-pot (1DS) and D-pot (the control), respectively. The SPAD values also showed no significant differences and ranged from 39.6 to 40.5. However, the plant height in C-pot was 44.0 cm and significantly ($P < 0.05$) lower than that in A-pot (49.6 cm), B-pot (48.1 cm), and D-pot (49.9 cm). The final of measurement at this stage showed the oxidation status by ORP; only B-pot, which was treated with split fertilizer,

was still in an oxidized or aerobic state (ORP > 300 mV) (Szögi et al., 2004). A-pot, D-pot, and E-pot were in moderately reduced or anaerobic states (100–300 mV) (Szögi et al., 2004), C-pot was in reduced states (–100 < ORP < 100 mV) (Szögi et al., 2004). These results indicated that B-pot may have a higher NH_3–N content than the other pots.

After the panicle initial stage (42 DAT), there was a significant ($P < 0.05$) difference in the plant height that could be separated into two groups. The first group consisted of A-pot (64.8 cm) and B-pot (66.2 cm) plants, which were not significantly different from each in height but were significantly taller than plants in the second group. The second group consisted of C-pot (62.1 cm) and D-pot (60.8 cm) plants, which were not significantly different from each other in height. The panicle number for C-pot (34.6 stems) and D-pot (33.2 stems) plants was not significantly different from that in B-pot (38.6 stems) plants but was significantly ($P < 0.05$) different from that for A-pot (45.0 stems) plants. A-pot and B-pot plants were not significantly different from each other. There was no significant difference in the SPAD values, which ranged from 28.3 to 39.6. At this stage, B-pot, C-pot, and D-pot were in highly reduced states (ORP < –100 mV). A-pot was still in a reduced state (–100 < ORP < 100 mV), and only E-pot (ORP > 300 mV), which had no plant, was in an oxidized or aerobic state (Szögi et al., 2004). The growth duration, which were the tallest, and the stem number and SPAD value of B-pot plants, indicate that the difference may be because of oxidation status, an indicator of the NH_3–N content (Szögi et al., 2004), in flood soil from the tillering stage.

Table 2.4. Dates of stages, differences in air temperatures and solar radiations inside and outside the greenhouse, growth durations, yields, and harvest indices in controlled pot cultivation tests (Mean ± SD, n = 5)

Pot	A-pot	B-pot	C-pot	D-pot	E-pot
Tillering stage	Jul 30, (20 DAT)				
ΔT (°C)	3.34				
ΔS (lux)	1124				
Height (cm)	49.60 ± 4.44[a]	48.10 ± 1.85[a]	44.00 ± 2.74[b]	49.90 ± 1.34[a]	-
Stem number (stem/hill)	12.80 ± 1.30[a]	9.20 ± 4.82[a]	9.60 ± 1.14[a]	11.20 ± 2.86[a]	-
SPAD value	40.00 ± 1.26[a]	39.58 ± 1.10[a]	39.76 ± 3.43[a]	40.54 ± 1.73[a]	-
ORP	222	511	45	163	115
Panicle initial stage	Aug 21 (42 DAT)				
ΔT (°C)	3.44				
ΔS (lux)	1630				
Height (cm)	64.80 ± 1.75[a]	66.20 ± 2.47[a]	62.10 ± 1.67[b]	60.80 ± 1.92[b]	-
Stem number (stem/hill)	45.00 ± 6.44[a]	38.60 ± 4.51[ab]	34.60 ± 3.99[b]	33.20 ± 3.90[b]	-
SPAD value	36.66 ± 3.85[a]	38.62 ± 4.18[a]	39.62 ± 1.34[a]	28.32 ± 2.67[a]	-
ORP	–90.00	–154.50	–135.00	–257.00	353.5
Flowering date	Sep 8 (60 DAT)				

Table 2.4. Dates of stages, differences in air temperatures and solar radiations inside and outside the greenhouse, growth durations, yields, and harvest indices in controlled pot cultivation tests (Mean ± SD, n = 5) (cont.)

Pot	A-pot	B-pot	C-pot	D-pot	E-pot
Ripening stage	Oct 9 (91 DAT)				
ΔT (°C)	3.1				
ΔS (lux)	1255				
Height (cm)	82.50 ± 2.45[a]	82.00 ± 2.40[a]	80.60 ± 2.04[a]	71.90 ± 1.25[b]	-
Panicle number	27.40 ± 2.51[a]	29.40 ± 1.95[a]	27.60 ± 2.30[a]	18.20 ± 1.48[b]	-
Panicle length (cm)	18.80 ± 1.15[a]	18.20 ± 0.76[a]	18.20 ± 1.30[a]	14.90 ± 1.29[b]	
SPAD value	22.44 ± 1.47[a]	25.50 ± 2.75[b]	22.02 ± 2.72[a]	13.84 ± 1.17[c]	-
ORP	–170.0	–198.2	–144.0	–226.0	190.0
Harvest date	Oct 14 (96 DAT)				
Yield (t/ha)					
Grain	7.32 ± 0.19[a]	8.23 ± 0.24[b]	7.30 ± 0.52[a]	3.65 ± 0.22[c]	-
Straw	6.45 ± 0.29[a]	6.6 ± 0.45[a]	5.87 ± 0.59[b]	3.95 ± 0.27[c]	-
Total	13.77 ± 0.02[a]	14.82 ± 0.06[b]	13.17 ± 0.11[a]	7.60 ± 0.01[c]	-
Harvest index	0.53 ± 0.02[a]	0.56 ± 0.02[a]	0.55 ± 0.01[a]	0.48 ± 0.03[b]	

Note: A-pot = applied chemical fertilizer, B-pot = periodic application of digested slurry, C-pot = one-time application of digested slurry, D-pot = no applied fertilizer, E-pot = no fertilizer and no plant; DS = digested slurry, ΔT = difference in air temperature inside and outside the greenhouse, ΔS = difference in solar radiation inside and outside the greenhouse, and DAT = days after transplantation. Alphabets in each row represent the $LSD_{0.05}$ for mean values comparison.

At the ripening stage (90 DAT), the plant height and panicle number and length of A-pot, B-pot, and C-pot plants were significantly ($P < 0.05$) higher than those of D-pot plants, but not in the SPAD values. The SPAD value of B-pot (25.5) plants was significantly ($P < 0.05$) higher than that of the plants in other pots, while the SPAD values of A-pot (22.4) and C-pot (22.0) plants were significantly ($P < 0.05$) higher than D-pot (13.8) plants. However, the panicle number (29.4) and plant height of B-pot (82.0 cm) plants was the highest, however, the panicle length was same as that in C-pot (18.2 cm) plants. The OPR values of all treatments were lower than –100 mV (anaerobic and highly reduced), except in the case of E-pot, which still showed a positive value.

For grain (includes rice husk) and straw yields, the grain yield of B-pot (8.23 t/ha) plants was significantly ($P < 0.05$) higher than that of A-pot (7.32 t/ha) plants. The grain yield of C-pot (7.30 t/ha) and D-pot (3.65 t/ha) plants was significantly ($P < 0.05$) lower than that of plants in the other pots. The straw yield of B-pot (6.59 t/ha) plants was the highest but was not significantly different from that of A-pot (6.45 t/ha) plants. C-pot (5.87 t/ha) and D-pot (3.95 t/ha) plants had significantly different straw yields from each other and from the other plants. Therefore, HI of B-pot (0.56) plants was the highest, but was not significantly ($P < 0.05$) different from that of C-pot (0.55) or A-pot (0.53) plants.

(2) Nitrogen use efficiency

The N uptake during cultivation in the controlled pot cultivation tests is shown in Figure 2.5. Before application of fertilizers at the panicle initial stage (40 DAT), A-pot plants exhibited the highest N uptake but later it was similar to B-pot plants until 8 weeks after transplantation. N uptake in C-pot plants was lower than that in either A-pot or B-pot plants.

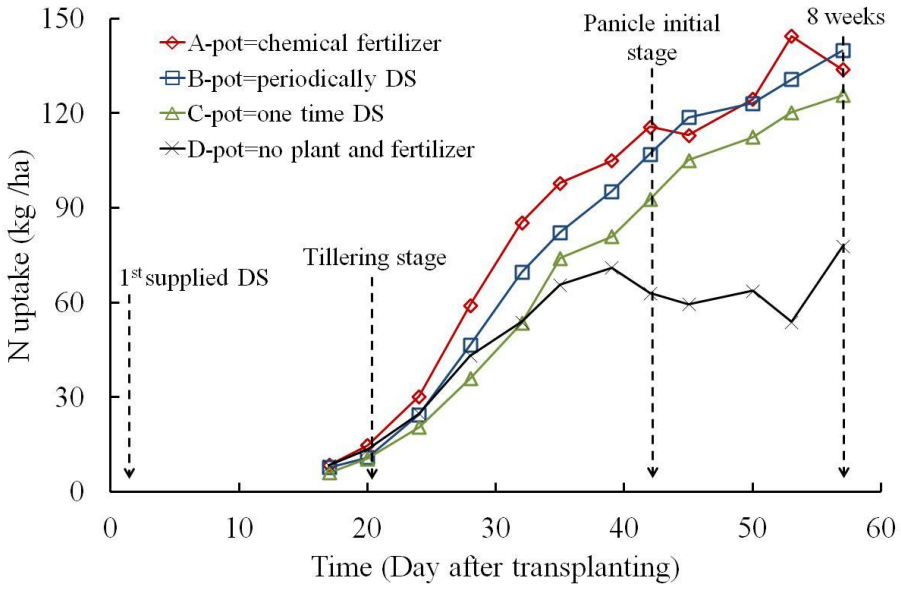


Figure 2.5. N uptake (calculated by Eq. 2.1) from 2 weeks until 8 weeks during cultivation in controlled pot cultivation tests.

Table 2.5 shows the gained N uptake, PE, RE, and AE in controlled pot cultivation tests at 8 weeks after transplantation. The gained N uptake value of B-pot (62.59 kgN/ha) plants was the highest. The value was not significantly different from A-pot (56.31 kgN/ha) plants but was significantly different from C-pot (48.53 kgN/ha) plants, with a level of significance of 0.2. These results demonstrated that plants absorb N well from fertilizers applied periodically.

PEs were 6.85, 7.64, and 8.23 kg/kgN for A-pot, B-pot, and C-pot plants, respectively. PE of C-pot plants was the highest; however, there were no significant differences between each experimental section.

REs were significantly different only between B-pot and C-pot ($P < 0.2$) plants. REs of the experiment were sorted by ascending order and were 40.45%, 46.93%, and 52.16% for C-pot, A-pot, and B-pot plants, respectively.

B-pot plants had significantly higher AE (3.82 kgN/kgN, $P < 0.2$) than C-pot (lowest AE, 3.04 kgN/kgN) and A-pot (3.06 kgN/kgN) plants, but there was no significant difference between AEs of C-pot and A-pot plants.

Table 2.5. Gained N uptake, physiological efficiency, fertilizer N-recovery efficiency, and agronomic efficiency in controlled pot cultivation tests

Pot Exp.	Gained N uptake (kgN/ha)	N use efficiency		
		PE	RE (%)	AE
A-pot	56.31 ± 12.42^{ab}	6.85 ± 1.89^{a}	46.93 ± 10.35^{ab}	3.06 ± 0.16^{a}
B-pot	62.59 ± 14.70^{a}	7.64 ± 1.70^{a}	52.16 ± 12.25^{a}	3.82 ± 0.20^{b}
C-pot	48.53 ± 18.09^{b}	8.23 ± 2.83^{a}	40.45 ± 15.07^{b}	3.04 ± 0.43^{a}

Note: A-pot = application chemical fertilizer, B-pot = periodic application of digested slurry, C-pot = one-time application of digested slurry, PE = physiological efficiency, RE = fertilizer N recovery efficiency, and AE = agronomic efficiency. Alphabets in each row represent the $LSD_{0.2}$ for mean values comparison.

2.3.2 Rice cultivation test in actual wet rice fields in Yamaga City

(1) Growth duration and yield

Table 2.6 shows dates of stages, growth durations, yields, and HIs in actual wet rice fields. At the tillering stage, the PDS plot plants showed poor results for the plant height (27.0 cm) and stem number (15.6 stems/hill) than CF and 1DS plot plants. The CF plot plants were the tallest at this stage (31.0 cm), while those in the 1DS plot had the highest stem number (19.1 stems/hill).

At the panicle initial stage, the stem number of the PDS plot (39.4 stems/hill) plants increased more rapidly than those of the CF (36.9 stems/hill) and 1DS (35.9 stems/hill) plot plants. Furthermore, the leaf color of the PDS plot plants had the same value as those of the CF plot (4.5) plants but more than that of the 1DS (4.0) plants. CF plots had the tallest (59.3 cm) plants, while PDS and 1DS plots had plants with similar heights, 52.7 and 53.0 cm, respectively.

At the ripening stage, panicle number and length (31.0 panicles/hill, 18.9 cm, respectively) were the highest for PDS plot plants, while CF and 1DS plot plants had 30.4 and 28.4 panicles/hill and 15.9 and 18.4 cm panicles, respectively. CF plots had the tallest plants at 113.2 cm, while PDS and 1DS plots had plants of similar height, 93.5 and 91.4 cm, respectively.

After harvesting, PDS plot plants showed greater straw (5.40 t/ha) and grain (6.79 t/ha) yields than CF and 1DS plot plants, but these was no significant difference between 1DS (6.68 and 4.89 t/ha of grain and straw yields, respectively) and CF (6.51 and 4.86 t/ha of grain and straw yields, respectively) plot plants. The average value for HIs for PDS, 1DS, and CF plot plants was not significantly different at 0.56, 0.58, and 0.57, respectively.

(2) Nitrogen use efficiency

Figure 2.6 shows N uptake in actual wet rice fields. Equation 2.1, revealed that the N uptake of 1DS plots was lower than that of CF and PDS plots around 1 month after transplantation. N uptake of CF and PDS plot plants was similar, although the N uptake of PDS plot plants was lower than that of CF plot plants, but most likely for the final stage.

Table 2.6. Dates of stages, growth durations, yields, and harvest indices in actual wet rice fields (Mean ± SD, n = 2)

Site	CF	PDS	1DS
Tillering stage	Jul 15 (24 DAT)		
Height (cm)	31.00 ± 2.29[a]	26.95 ± 2.01[b]	26.95 ± 1.73[b]
Stem number (stem/hill)	17.60 ± 5.89[NS]	15.55 ± 4.94[NS]	19.10 ± 5.89[NS]
Panicle initial stage	Aug 4 (44 DAT)		
Height (cm)	59.33 ± 4.78[NS]	52.65 ± 4.52[NS]	53.00 ± 4.78[NS]
Stem number (stem/hill)	36.85 ± 3.34[NS]	39.35 ± 8.10[NS]	35.85 ± 4.78[NS]
Leaf color (CS)	4.50 ± 0.71[NS]	4.5 ± 0.71[NS]	4.00 ±0 .71[NS]
Flowering date	Aug 26 (66 DAT)		
Ripening stage	Oct 3 (104 DAT)		
Height (cm)	113.18 ± 2.85[a]	93.49 ± 4.16[b]	91.37 ± 2.62[b]
Panicle number	30.35 ± 4.03[NS]	30.95 ± 5.77[NS]	28.40 ± 3.62[NS]
Panicle length (cm)	15.87 ± 1.58[a]	18.89 ± 0.99[b]	18.37 ± 0.92[b]
Harvest date	Oct 7 (108 DAT)		

Table 2.6. Dates of stages, growth durations, yields, and harvest indices in actual wet rice fields (Mean ± SD, *n* = 2), (cont.)

Site	CF	PDS	1DS
Yield (t/ha)			
Grain	6.51 ± 0.03^{NS}	6.79 ± 0.05^{NS}	6.68 ± 0.01^{NS}
Straw	4.86 ± 0.00^{NS}	5.40 ± 0.04^{NS}	4.89 ± 0.01^{NS}
Total	11.37 ± 0.06^{b}	12.19 ± 0.09^{a}	11.57 ± 0.03^{b}
Harvest index	0.57 ± 0.01^{NS}	0.56 ± 0.01^{NS}	0.58 ± 0.00^{NS}

Note: CF = application chemical fertilizer, PDS = periodic application digested slurry, 1DS = one-time application digested slurry, DS = digested slurry, and DAT = days after transplantation. Alphabets in each row represent the $LSD_{0.05}$ for mean values comparison.

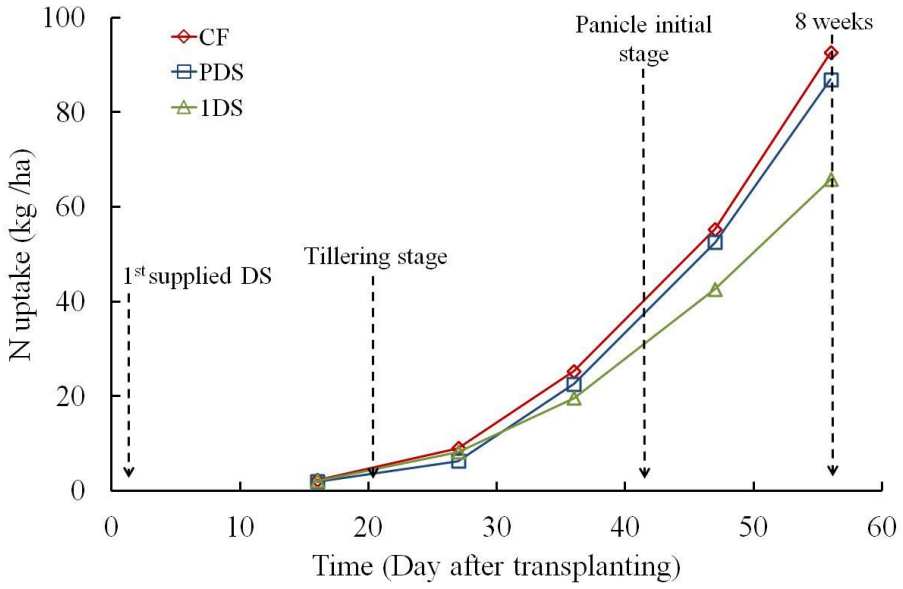


Figure 2.6. N uptake (calculated by Eq. 2.1) from 2 weeks until 8 weeks during cultivation in actual wet rice fields.

2.4 Conclusion

The controlled pot cultivation tests and in actual wet rice fields in Yamaga City were conducted to study difference in the effects between different methods of application of digested slurry (PDS and 1DS) for rice cultivation.

Periodic application of DS from methane fermentation with irrigation water to a wet rice field as a topdressing produced higher biomass yields than fertilizer applied as a basal dressing in PDS and was not different from fertilizer applied as a basal dressing in 1DS. Furthermore, PDS as a topdressing had a higher AE than fertilizer applied as a basal dressing, and 1DS as a topdressing had a higher PE than fertilizer applied as a basal dressing.

In N uptake, both experiments showed that PDS allows plants to absorb more N than 1DS, and this fact can be observed from the amount of N uptake by rice plants in Figures 2.3 and 2.4 and Table 2.5. The absorption capacity of plants and gained N uptake was 62.59 and 48.53 kgN/ha (Table 2.5) in PDS and 1DS, respectively, during the controlled pot cultivation tests. These results were similar to the actual wet rice field tests in Yamaga City. The reasons for these results may be that fertilizer applied as a basal dressing was mixed better than fertilizer applied as a topdressing, and thus, plant absorption of the applied fertilizer was faster. When the frequency of application is considered, PDS as a topdressing demonstrated a higher N uptake than 1DS as a topdressing. Furthermore, PDS may decrease nitrification and leaching losses because of the limited ability to absorb and assimilate nutrients in rice roots at transplantation.

CHAPTER 3

Basic Properties and Qualities Changes during Storage on Rice Straw

3.1 Introduction

Most agricultural product undergoes strong degradation in a few months after harvest (Brown, 2004). Therefore, preserving rice straw for periods in suitable storage conditions of a year or even longer is important and requested. In storage, the physical and chemical properties of straw deteriorate due to loss of nutrient and water in respiration process. Temperature is one factor that affects to respiration rate and preservation of postharvest life in storage (Thomson, 1998). Shapes of straw for storage are following; one is normal shape another is cut shape that means for storage in cubing form and milled shape in case of industrial using.

The objectives of this study were to compare the effect of 4 storage temperatures (10°C, 20°C, 30°C and ambient temperature) and 3 shapes of rice straw (untreated, cut and milled) on nitrogen, carbon, moisture, ash and respiration rate. This study was conducted 2 harvest years. The first harvest, rice straw would be stored 6 months and 4 months for the second harvest year.

3.2 Materials and methods

To study basic properties on rice straw for biomass resources the effects of size, temperature and duration time for storage of Hino Hikari were investigated by using 3x4x6 factorials in CRD with three levels of shape that is normal shape (untreated straw) as shown in Figure 3.1, cubing shape (cut straw) as shown in Figure 3.2, and milled shape (milled straw) as shown in Figure 3.3. Three temperatures were controlled by incubators

(10°C, 20°C, and 30°C), and controller temperature was ambient condition. This study was conducted 2 harvest years, the first harvest year was on 2008 to 2009 with storage times 1, 2, 3, 4, 5, and 6 months and the second time was on 2009 to 2010 with storage times 1, 2, 3, and 4 months. The experiments in second harvest year were controlled humidity in the incubators by a dehumidifier.

The rice straw samples were determined; moisture content, total nitrogen content, total carbon content and ash content. Moisture content was examined before storage until the end of experimental month. Total nitrogen content, total carbon content and ash content were determined every 2 to 4 weeks after storage until the end of experiments. Total nitrogen and total carbon contents were analyzed by weight percentage by the Kjeldahl method and Dichromate Redox method, respectively.

Figure 3.1. Untreated straw for using in study basic properties on rice straw.

Figure 3.2. Cut straw for using in study basic properties on rice straw.

Figure 3.3. Milled straw for using in study basic properties on rice straw.

Besides, the cut straw was measured respiration rate of carbon dioxide (CO_2) by using Automatic CO_2 Analyzer EIR-200S with three levels of temperatures (10, 20, and 30°C). Cut straw of 150 g was put into plastic box and this box was put in Automatic CO_2 Analyzer EIR-200S to control box temperature and measure CO_2 in the box. The initial and the end weight of cut straw were measured for determine loss weight.

3.3 Results and discussion

3.3.1 Sample conditions

The rice straw was separated to 3 sizes; untreated straw size, cut straw size, and milled straw size in both of harvesting year. For the first harvest year, untreated and cut straw were 750 and 255 mm of length, respectively and their density was 98 kg/m^3. For the milled straw, average particle diameter was 1.3 mm and 198.7 kg/m^3 of density. The second harvest year, length and density of untreated and cut straw were 775 and 382 mm, and 110 kg/m^3, respectively. For the milled straw, average particle diameter was 1.6 mm and 198.5 kg/m^3 of density.

3.3.2 Moisture content

The ranges of moisture content in the first and the second harvest year were 8.9% to 21.7% and 5.9% to 13.6%, respectively. From Figures 3.4 and 3.5, when compared both harvest year experiments, the experiments in the second harvest year had better classifies than the first harvest year. The reason that the experiments were controlled humidity on the second harvest year. However, both harvest years had results in the same way. That is, moisture content had significant difference at 99% of confidence level with storage time and temperature. Moisture content would be decreased when storage time increase in both experiments. For storage temperature, moisture content seemed decreased when temperature increase for the first harvest year, but they were clear that

moisture content would be decreased when temperature increase, except at 10°C and 20°C in the second harvest year. Moisture content reduced immediately on first month of storage in all of three sizes of rice straw and in both harvest years. Especially, at 30°C of storage temperature on the first harvest year, all sizes of straw had some fungus, thus they were stop after 4 months storage. Thus on the second harvest year, the experiments would be hold until 4 months of storage. Ambient condition affected to moisture content slightly. The reason that, the seasons of experiments was from winter to spring thus temperature was low from 2.1 to 22.0 (average 10.7) and 1.2°C to 19.7°C (average 9.03°C) in the first and the second harvest year, respectively. However, moisture content had no significant difference with size of straw.

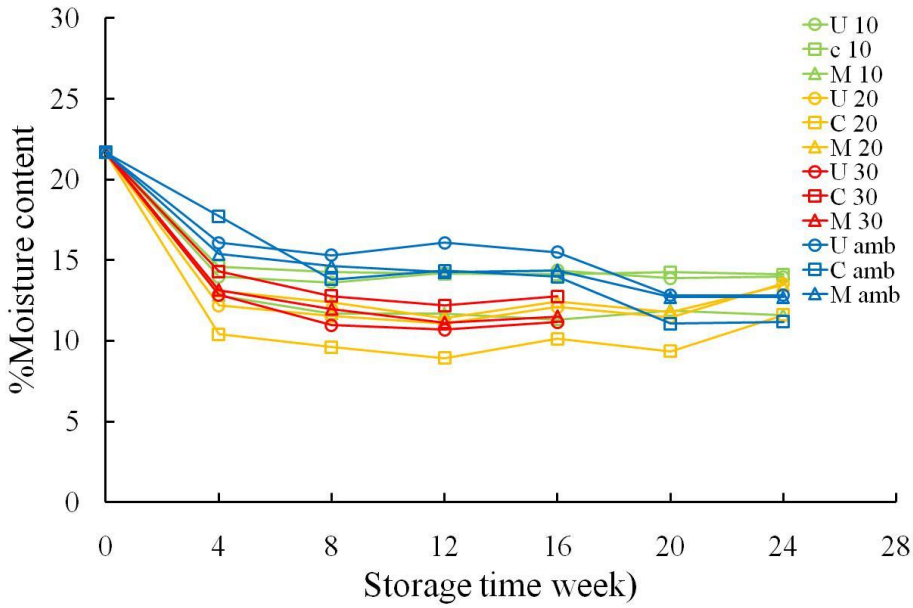


Figure 3.4. The moisture contents of rice straw in different storage times, temperatures, and sizes on the first harvest year.

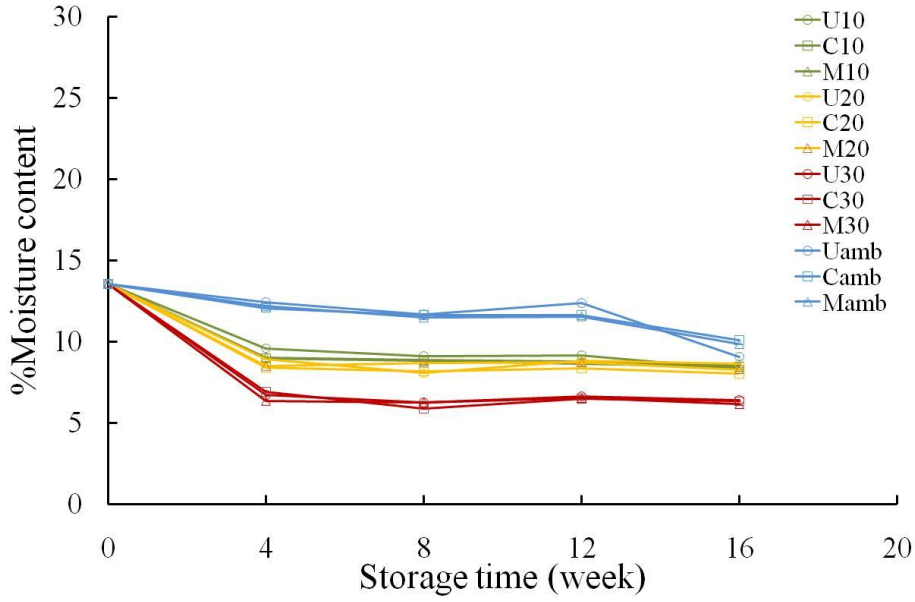


Figure 3.5. The moisture contents of rice straw in different storage times, temperatures, and sizes on the second harvest year.

3.3.3 Total nitrogen

Total nitrogen (TN) affected size, temperature and duration time in both harvest years. The ranges were 0.39%db to 0.64%db and 0.43%db to 0.67%db for the 1st and 2nd harvest year, respectively. The results showed that initial rice straw had the highest TN (the second harvest year) and increasing of duration time and temperature caused TN decreased in both of harvest years (Fig. 3.6 and 3.8). The reason was that, moisture (which decreased when storage time increase) and temperature are the major factors in the formation or degradation of organic matter such as TN (Wagai et al., 2008). For considered size of storage, there were not big differences in the second harvest year (Fig. 3.9). However, in the first harvest year, untreated straw had the highest TN, 0.55%db (Fig. 3.7) and significant difference with milled straw (0.52%db) and cut straw (0.46%db).

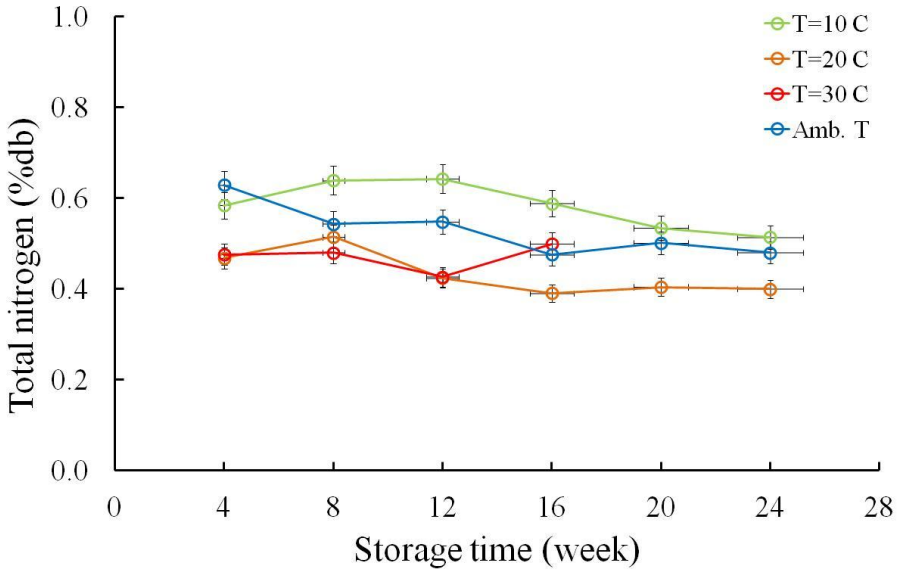


Figure 3.6. Total nitrogen of rice straw in different storage times and temperatures on the first harvest year.

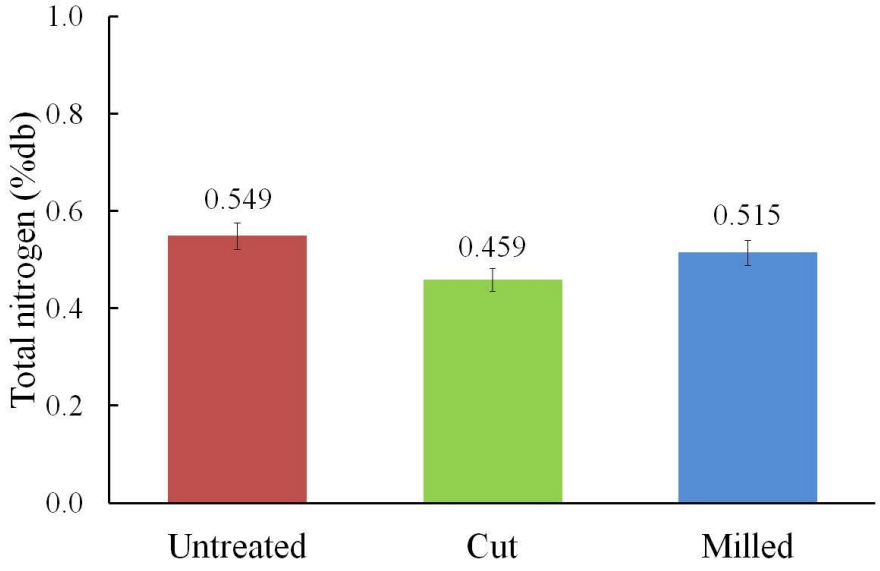


Figure 3.7. Total nitrogen of rice straw in different storage size on the first harvest year.

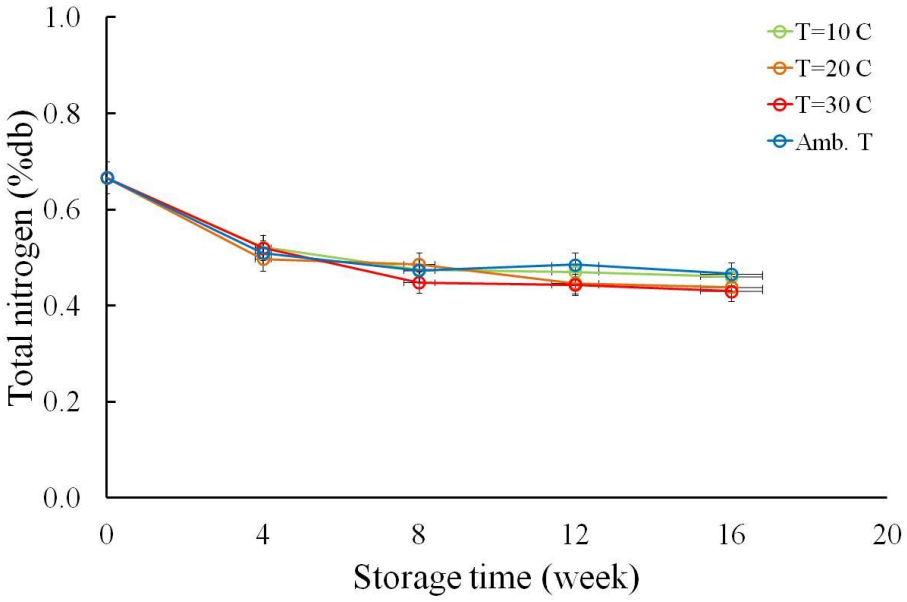


Figure 3.8. Total nitrogen of rice straw in different storage times and temperatures on the second harvest year.

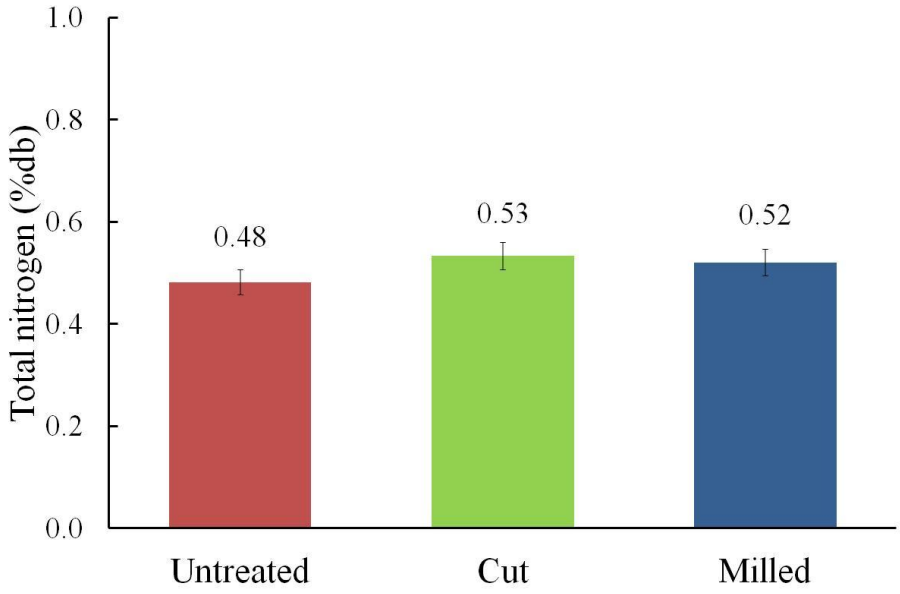


Figure 3.9. Total nitrogen of rice straw in different storage size on the second harvest year.

3.3.4 Total carbon

Experimental total carbon results (TC) were varied from 33.4%db to 42.3%db and 36.9%db to 42.4%db for the first harvest year (Fig. 3.10) and the second harvest year (Fig. 3.12), respectively. TC affected with storage time, it decrease when storage time increased. For the first harvest year, TC was high significant difference with storage temperature and a litter significant difference on the second harvest year. The reason time and temperature affected to TC as above mentioned in TN part, and the reason for the first harvest year had higher significant difference than the second harvest year was the initial moisture content on the first harvest year was higher than the second year. For storage size, it was not significant difference with TC in both harvest years (Figs. 3.11 and 3.13).

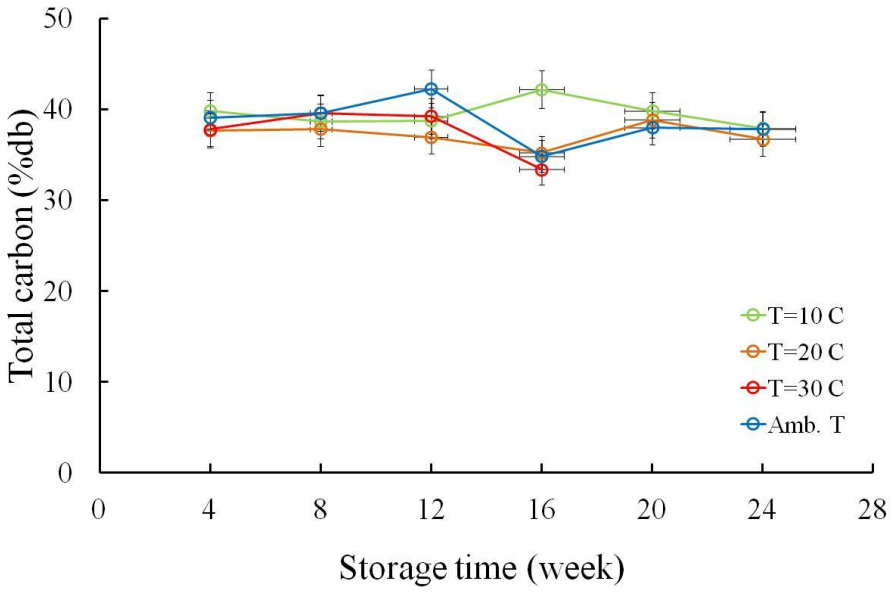


Figure 3.10. Total carbon of rice straw in different storage times and temperatures on the first harvest year.

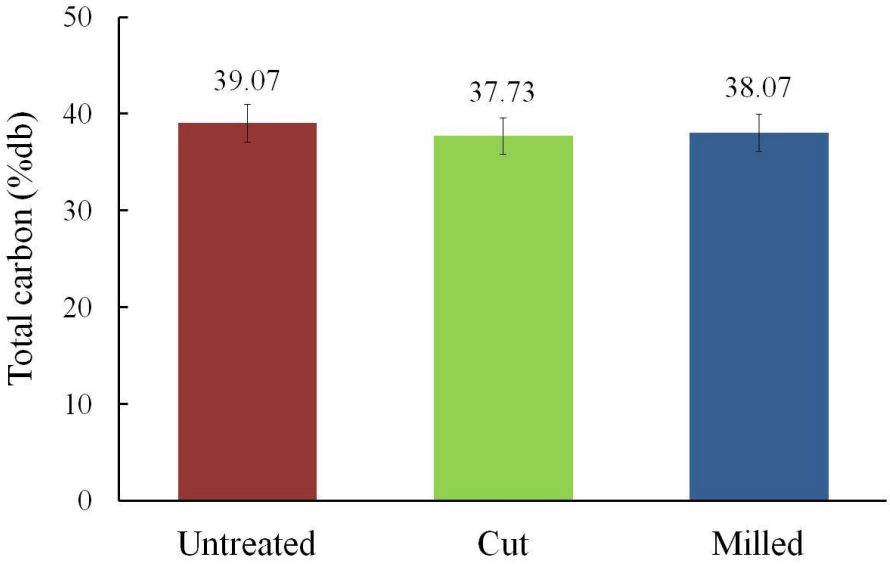


Figure 3.11. Total carbon of rice straw in different storage size on the first harvest year.

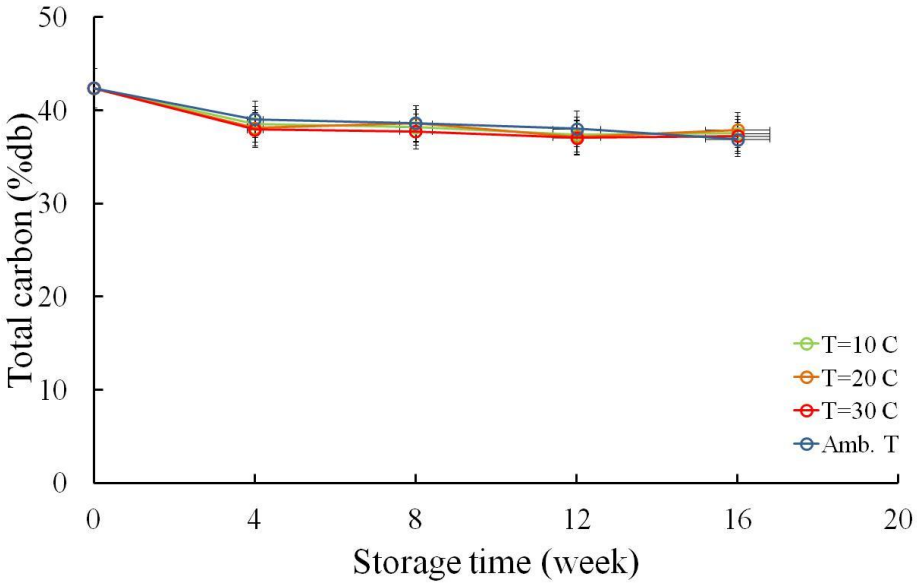


Figure 3.12. Total carbon of rice straw in different storage times and temperatures on the second harvest year.

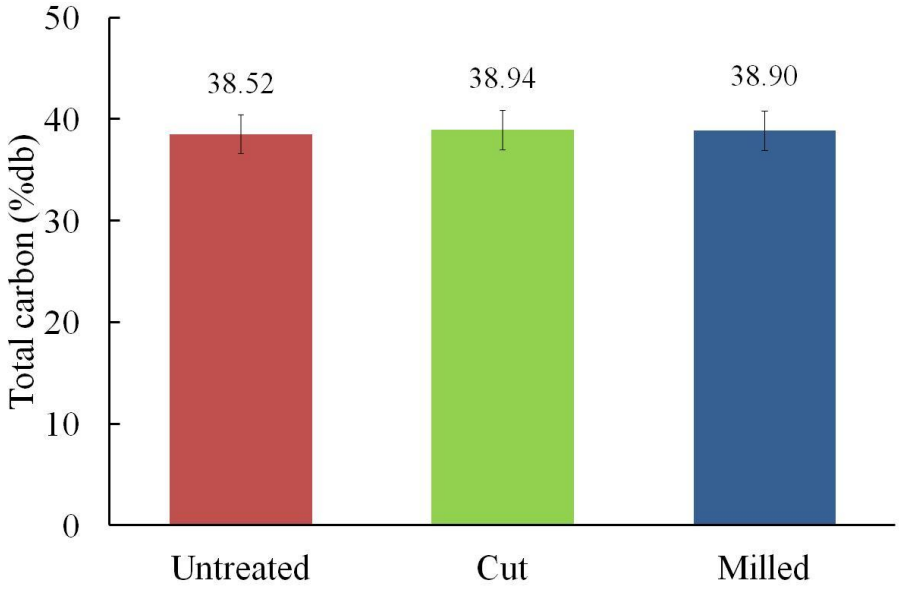


Figure 3.13. Total carbon of rice straw in different storage size on the second harvest year.

3.3.5 Ash concentration

For ash concentration, Tables 3.1 and 3.2 reviews ash concentrations in different storage sizes of rice straw, different storage temperatures and different storage times for the first and second harvest year, respectively. Ash concentration tended to rise when storage temperature and storage time increased, due to storage temperature and time affect decomposition to organic matter, thus rice straw may have high concentrate of inorganic matter, referred as ash. These effects were adverse with organic matter, thus tendency results of storage size were also opposite with TC results.

Table 3.1. Ash concentration of rice straw during storage on the first harvest year

Shape	Mean (%db)	Temperature (°C)	Mean (%db)	Time (month)	Mean (%db)
Untreated	13.65	Ambient	14.34	1	14.94
Cut	15.53	10	14.88	2	14.81
Milled	15.35	20	15.31	3	14.97
		30	13.69	4	14.30
				5	14.64
				6	14.84

Table 3.2. Ash concentration of rice straw during storage on the second harvest year

Shape	Mean (%db)	Temperature (°C)	Mean (%db)	Time (month)	Mean (%db)
Initial	14.47				
Untreated	14.15	Ambient	14.05	1	14.18
Cut	13.93	10	13.93	2	14.13
Milled	13.86	20	14.06	3	13.90
		30	13.89	4	13.98

3.3.6 Respiration rate of CO_2

When considered respiration rate of rice straw, loss weight and generated CO_2 of cut straw were measured at three levels of storage temperature (10°C, 20°C and 30°C). Figure 3.14 shows loss weight, rice straw had the highest of loss water at 30°C of storage temperature. Furthermore, CO_2 respiration rate (Fig 3.15) indicated that this temperature

(at 30°C) had the shortest time life when compared with other storage temperatures. It may be due to incrimination of respiration rate by higher temperature and lost water. As the results of loss weight and CO_2 respiration rate, at 10°C of storage temperature, qualities of cut straw may better than other conditions. There were low loss weight and long time of respiration at 10°C of storage temperature.

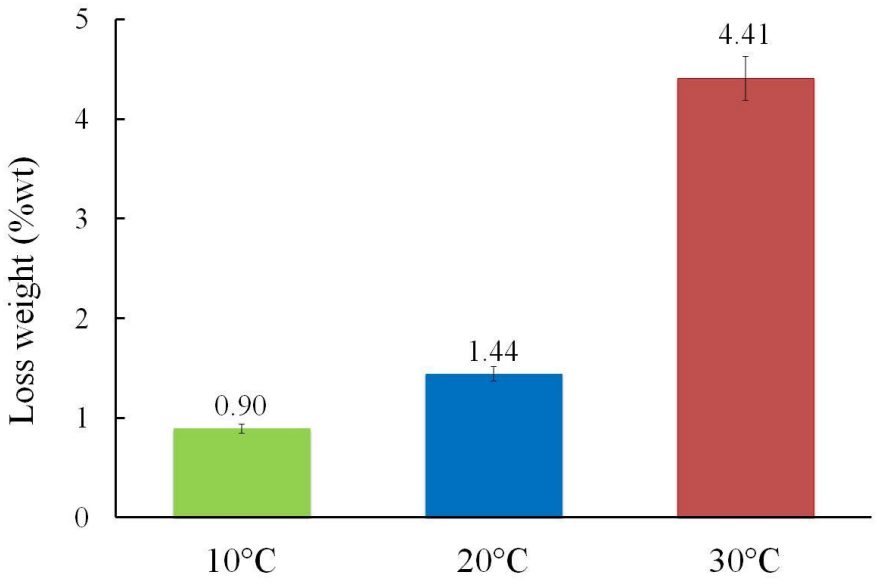


Figure 3.14. Loss weight (%) of straw on the first harvest year.

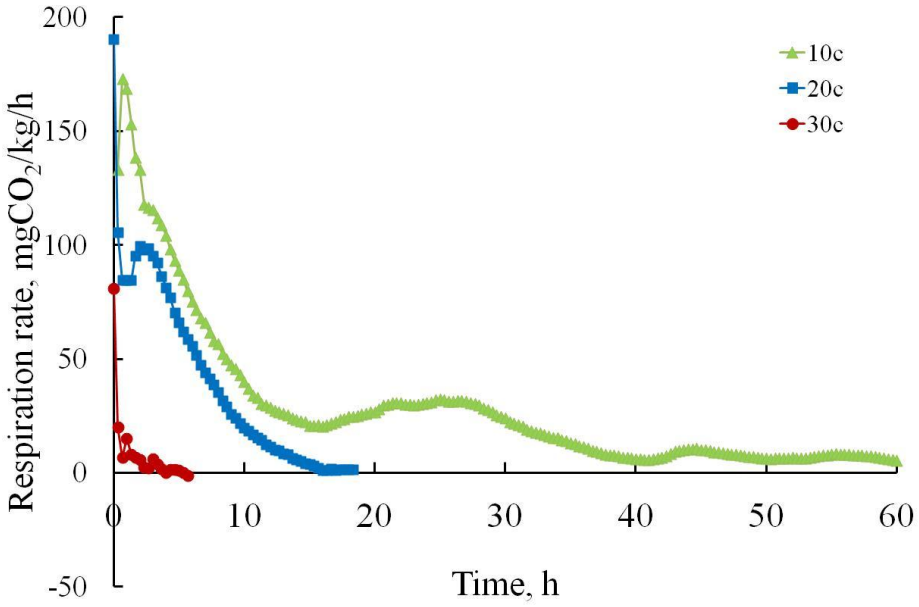


Figure 3.15. CO_2 respiration rate of cut straw on the different storage temperature.

3.4 Conclusion

For study effects of storage temperature, time and size on moisture, total nitrogen, total carbon, ash and respiration rate of rice straw, whole storage conditions affected rather on qualities of rice straw. Storage time and temperature increased, qualities would be decrease. Especially, temperature at 30°C affected more than other and duration time was stopped on 4 months in the first harvest year. However, storage time had high effect on the first month in both harvest years, after that, there was a bit difference.

CHAPTER 4

Development of a Calorimetric Method

by Using Thermodynamically Open System

4.1 Introduction

As mentioned in chapter 1, energy content is a important index to identify biomass as energy and a calorimeter with mass exchange or open system and with heat exchange or non-adiabatic, is one kind of calorimetric system to estimate the energy content by using mass and energy balance equations. To consider principles on estimation of energy content by the mass and energy balances or conservation for the open system, the mass and energy going into the combustion chamber must balance with the mass and energy coming out. The details were described in Cengel and Boles (2006) as below;

For the law of conservation of mass or the mass balance, when the process was considered steady state at the same time, control volume of a simple calorimeter, is given by,

$$\sum M_i = \sum M_e \tag{4.1}$$

In the same way of mass conservation, energy is conserved in a simple calorimeter. The energy coming into a system can be balanced with the energy coming out and the energy remain is shown in Eq. 4.2.

$$\sum E_i = \sum E_e + \sum E_{remain} \tag{4.2}$$

This study is aimed to develop the direct determination of energy content of biomass solid fuel from measurements of heat released, using the laws of conservation of mass and heat accompanied with the simple calorimeter or the thermodynamically open system. In this study, a calorimetric method by energy balance equations with collecting data for

heat input and output and the construction details of the open calorimeter was mainly presented.

4.2 Experimental apparatus and methodology

4.2.1 Sample preparation

In this study, rice straw was applied to estimate energy content and whose variety was Hino Hikari. Three different treatments were used to examine the simple calorimeter or the open system calorimeter (OSC). The first treatment was the original rice straw (OS), the second treatment was rice straw which had been stored for 4 months with untreated (US), and the last treatment was stored for 5 months after milling (MS). Moisture contents of samples were 13.55%, 10.44% and 8.68% for OS, US and MS, respectively. To burn in OSC, rice straw was crushed to small particle size whose average particle size was about 1.32 mm.

4.2.2 Construction details of an open system calorimeter

The open system calorimeter used in this study and a schematic of it are shown in Figures 4.1 and 4.2, respectively. Table 4.1 shows specifications of the system.

Main body of the simple calorimeter was built from diatomaceous earth. Sample was put in a small sieve tray which was on the stand under small bowl. The electrodes were connected from power supply to the small sieve tray with a nichrome wire as an igniter. Area between the small sieve and the stand was covered by aluminum foil to increase efficiency of heat transfer into the water. Under the stand, there was a tray to receive some particles of material which may fall from the small sieve tray and become unburned material. 100 ml of water was placed in the bowl to estimate energy output due to heat transfer to water (gained heat output). There are 8 fins inside the bowl to increase surface of gained heat. Three thermistors were set in the bowl for recording water

temperature and two thermistors were also set at wall, 50 and 100 mm from bottom of combustion chamber. Two air inlet lines were inserted through the top and the ends of lines were set under the small sieve tray to add oxygen to the ignition system. The top of combustion chamber had a hole for discharging flue gas and there was a thermistor for measuring flue gas temperature and a flow meter to measure gas flow rate. On the outside wall, there was the thermistor to measure surface temperature for estimating heat output through the wall.

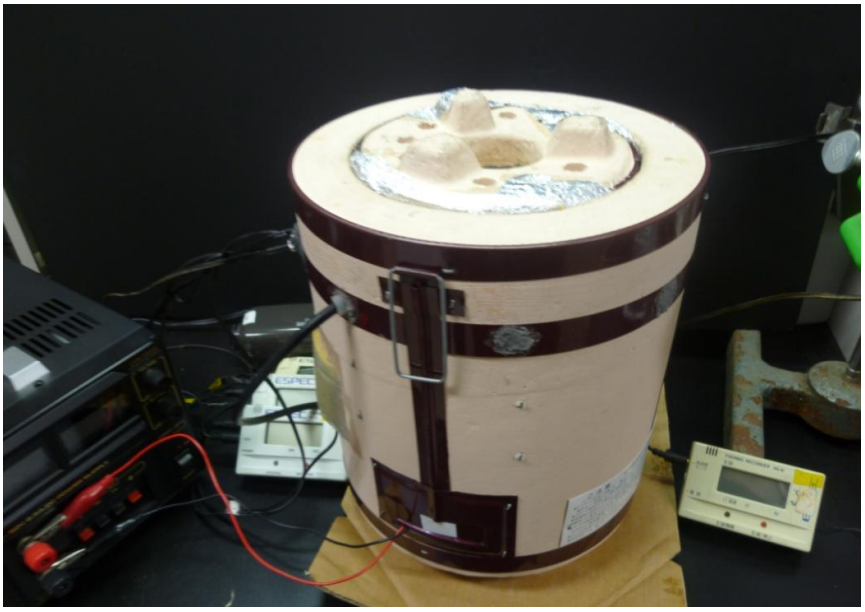


Figure 4.1. Open system calorimeter used.

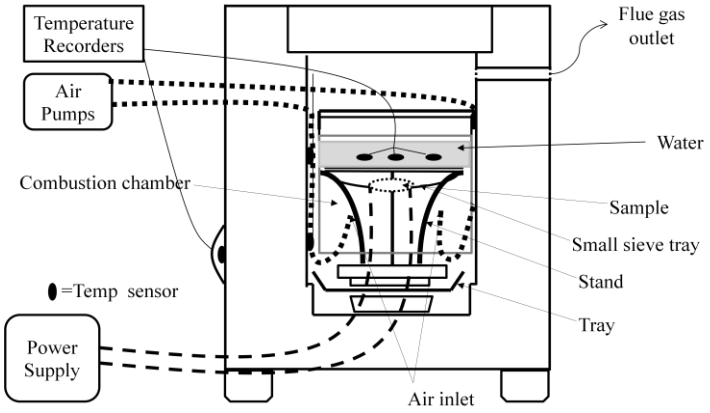


Figure 4.2. Schematic diagram of the calorimeter used.

Table 4.1. Specifications of the system

The OSC shape	Hollow cylinder
Dimensions	
- outer	∅220 × H235 mm
- inner	∅120 × H160 mm
Weight	5.5 kg
Body material	Diatomaceous earth

4.2.3 Mass and energy balances solution

In this study, energy content in a sample was determined by the mass and energy balance methods for biomass solid fuel. The details are follows,

(1) The mass balance solution

For the mass balance solution in the simple calorimeter, it was assumed that the processes were in the steady state. From Eq. 4.1 and considered OSC as a system obtains,

$$M_s + M_a = M_f + M_{ub} + M_{inc} + M_{cw} + M_o \quad (4.3)$$

where, M_s, M_{ub}, M_{inc} and M_{cw} achieved from measuring the mass. M_a and M_f were considered and calculated by ultimate analysis and theoretical (stoichiometric) air fuel ratio and excess air supplied during the process. Finally, M_o was estimated from the difference of mass input and mass output.

For material as a system and from Eq. 4.1, we obtain,

$$M_s = M_b + M_{ub} + M_{inc} \quad (4.4)$$

where, M_s, M_{ub} and M_{inc} obtained from weight. M_b was calculated from the difference of M_s, M_{ub} and M_{inc}.

(2) The energy balance solution

The energy balance solution could be measured by measuring all the energy input and output occurring in OSC using following principles described. However, in this study water vapour which was produced from hydrogen in material, moisture present in material and air during the combustion was not considered in energy output due to dry flue gas. The energy outputs due to hydrogen and moisture in material, and air were separately considered as a wet flue gas.

Therefore the various energy inputs and outputs occurring in the calorimeter consisted of,

- Energy input due to energy of fuel
- Energy input due to power supply
- Energy output due to transfer to water (gained heat output)
- Energy output due to dry flue gas (flue gas output)
- Energy outputs due to evaporation of water formed from hydrogen (H_2) in material, moisture present in material and air during the combustion (condensed water output)

- Energy output due to surface radiation, convection and conduction (surface output)

- Energy output due to unburned material (unburned output)

- Energy output due to incomplete burned material (incomplete combustion output)

- Energy output due to unaccounted (other output)

They were represented an entire input and output energy flow in the OSC in Figure 4.3 and were derived as Eq. 4.5.

$$E_s+E_p=E_g+E_f+E_{cw}+E_{ub}+E_{inc}+E_{surf}+E_o \quad (4.5)$$

To achieve results from Eq. 4.5, data was collected from the OSC, and Table 4.2 shows summary the data required for calculation of energy content by using the simple calorimeter.

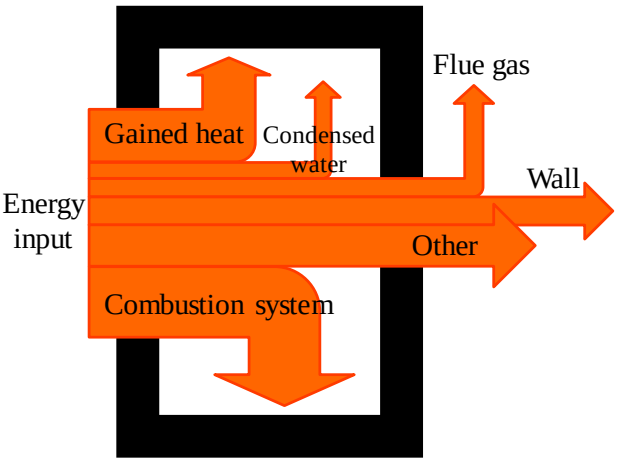


Figure 4.3. Energy balance for a simple calorimeter.

Table 4.2. Summary the data required for calculation of energy content by using the simple calorimeter

The data required for calculation	Unit
- O_2, N_2, CO_2 and CO in flue gas	%
- Condensed water at bottom of bowl	
- Flue gas temperature	°C
- Flue gas flow rate	m^3/min
- Inside and outside wall temperatures	°C
- Ambient temperature	°C
- Air flow rate	m^3/min
- Water temperature	°C
- Carbon content in uncompleted sample	%
- Electricity	

The details and procedures for calculating energy content by using the mass and energy balances method are given in Eqs. 4.6 to 4.15 as below,

(1) Energy input due to energy of fuel sample

$$E_s = M_s \times HHV \tag{4.6}$$

(2) Energy input due to electricity

$$E_p = I \times V \times t \tag{4.7}$$

(3) Energy output due to transfer to water

$$E_g = M_w \times C_{p,w} \times (\Delta T_w) + M_w \times L_V \tag{4.8}$$

(4) Energy output due to dry flue gas

$$E_f = M_f \times C_{p,f} \times (T_f - T_a) \tag{4.9}$$

(5) Energy outputs due to evaporation of water formed from H_2 in material, moisture present in material and air during the combustion

$$E_{cw}=M_{cw}\times L_{V,w} \tag{4.10}$$

where, $L_{V,w}$ = 2257.1 kJ/kg (Cengel and Boles, 2006)

(6) Energy output due to surface

(i) Radiation

$$E_{rad}=A_o\times\varepsilon\times\sigma\times\left(T_{surf1}^4-T_a^4\right) \tag{4.11}$$

(ii) Convection

$$E_{conv}=A_o\times h\times\left(T_{surf1}-T_a\right) \tag{4.12}$$

where, $h = 1.42 \times \left(\frac{\Delta T}{L_1}\right)^{1/4}$ (Holman, 1986)

(iii) Conduction

$$E_{cond}=-2\times\pi\times k\times L_2\times\frac{(T_{surf1}-T_{surf2})}{\ln(R_1/R_2)}, \tag{4.13}$$

where, k = 0.06 $Wm^{-1}K^{-1}$

(7) Energy output due to unburned material

$$E_{ub}=M_{ub}\times HHV \tag{4.14}$$

(8) Energy output due to incomplete combustion

$$E_{inc}=M_{inc}\times\%C_{inc}\times HHV_C \tag{4.15}$$

(9) Energy output due to unaccounted

This energy output was estimated by calibrated known values.

4.3 Results and discussion

The energy content of rice straw was examined by using OSC accompanied with the mass and heat balances. Table 4.3 shows the results of the mass balance for rice straw using OSC.

From Table 4.3, total of mass inputs (M_s and M_a) expressed to the sum of M_f, M_{ub}, M_{inc}, M_{cw}.and M_o, whereas M_s was equal to sum of M_b, M_{ub} and M_{inc}. The amount of burned straw (M_b) was 0.090, 0.110 and 0.180 g. M_{inc} and M_{ub} referred to the amounts of incomplete combustion and unburned straw in the combustion chamber, where M_{inc} was 0.046, 0.070 and 0.108 g, and M_{ub} was 0.034, 0.020 and 0.032 g for OS, US, and MS, respectively. These results show the ratio of the amounts of unburned and incomplete combustion to total amount of straw in OSC was around 0.55. However, there amounts would be considered with the amount of carbon content for estimating the remained energy in the energy balance.

To determine the heating value of the sample, the results from Table 4.3 were applied to the energy balance equations. Table 4.4 shows results energy balance for rice straw using OSC and Table 4.5 shows ratio of energy output in each part of the open system calorimeter. To calculating energy output due to heat transfer to water, due to maximum temperature of water in the bowl (31.6°C to 33.9°C) was lower than boiling temperature of water, thus latent heat of vaporization in Eq. 4.8 was not considered in E_g.

Table 4.3. Summary of mass balance for rice straw using open system calorimeter

Input/Output Parameter	OS	US	MS
Mass input			
M_s	0.170	0.200	0.320
M_a	15.814	16.080	16.018
Total input	*15.984*	*16.280*	*16.338*
Mass output			
M_f	15.876	16.154	16.137
M_{ub}	0.034	0.020	0.032
M_{inc}	0.046	0.070	0.108
M_{cw}	0.023	0.021	0.028
M_o	0.005	0.015	0.033
Total output	*15.984*	*16.280*	*16.338*
M_b	0.090	0.110	0.180

Unit used: g (gram)

From Table 4.4, the energy output due to heat transfer to water (E_g) had highest output for OS and US, and the energy output due to incomplete combustion had highest for MS. However, after looking at the combined energy output in each part, the results in all of energy outputs had the same tendency. The energy output from the combustion system which combined energy output due to the unburned (E_{ub}) and the incomplete combustion (E_{inc}) had the highest output in all samples on the simple calorimeter with 37.51%, 36.35%, and 40.17% of total output for OS, US and MS, respectively, and average was 38.01% which agreed with results in the part of mass balance. The energy output due to

transfer to water (E_g) was the second highest with 27.25%, 30.27% and 22.71% of total output for OS, US and MS, respectively, and average was 26.74%.

Table 4.4. Summary of energy balance for rice straw using open system calorimeter

Input/Output Parameter	OS	US	MS
Energy input			
E_s	1978.5	2513.4	4190.2
E_p	535.7	429.0	418.3
Tot input	2514.2	2942.4	4608.5
Energy output			
E_g	685.2	890.5	1046.4
E_f	21.9	34.6	53.9
E_{cw}	52.0	47.1	62.7
E_{rad}	254.3	176.1	293.7
E_{conv}	99.4	67.3	111.9
E_{cond}	7.1	5.4	8.9
E_{inc}	547.4	818.2	1432.4
E_{ub}	395.7	251.3	419.0
E_o	451.2	651.9	1179.6
Tot output	2514.2	2942.4	4608.5

Unit used: Joule

Table 4.5. Ratio of energy output in each part of open system calorimeter

Part of the simple calorimeter	%Output			
	OS	US	MS	Avg
Gained heat output	27.25	30.27	22.71	26.74
Flue gas	0.87	1.17	1.17	1.07
Condensed water	2.07	1.60	1.36	1.68
Surface	14.35	8.46	9.00	10.60
Combustion chamber	37.51	36.35	40.17	38.01
Other	17.95	22.15	25.59	21.90

Unit used: %of total output

When comparing ratio of energy output due to heat transfer to water (gained heat output) and energy output due to unaccounted (other outputs) with weight of the sample, we found the ratios of other outputs increased when sample weight increased. The highest of other outputs was at 0.32 g of the sample weight which was 25.59% of total output. For the ratios of gained heat output, it had the highest at 0.2 g of sample weight, 30.27% of total output. The ratios of gained heat output would decrease when decreasing or increasing the sample weight, whereas at 0.32 g was 22.71% of total energy output and was the lowest of gained heat output (Fig. 4.4). From these results show using more sample weight would be achieved low gained heat output and high other outputs.

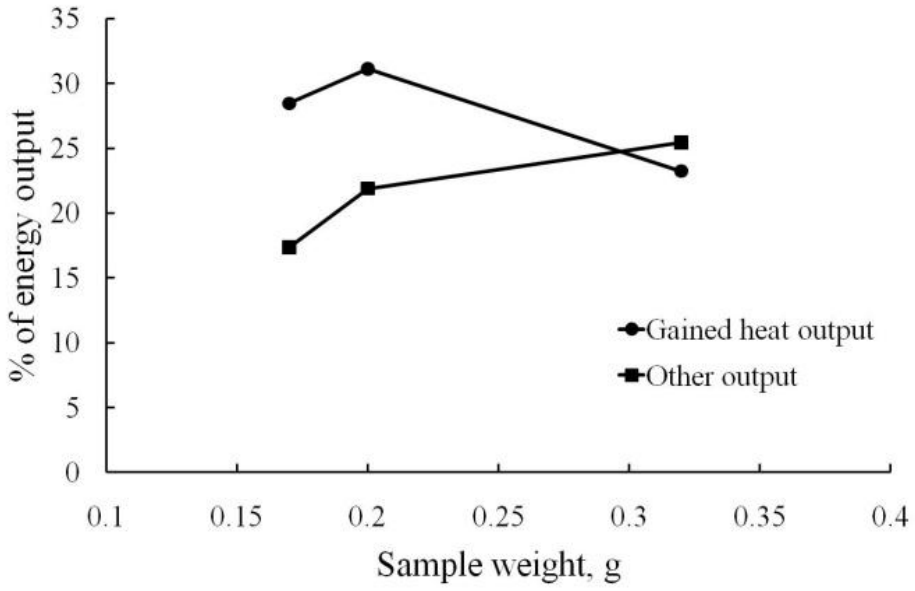


Figure 4.4. Comparison of gained heat output and other outputs in each sample weight.

4.4 Conclusion

The using the open system calorimeter to determine the energy content of biomass solid fuel accompanied with the mass and energy balances, the amount of sample weight was the important factor affecting energy output of OSC and achieved the best result at using 0.2 g of sample weight. Furthermore, estimation of other energy outputs (the unaccounted) which was a high value of energy output was examined from the calibrated known, was not an individual value in each examination which may be affected less or more to the simple calorimeter accuracy. Therefore, in the next study, to compare the heating value from the simple calorimeter with a commercial calorimeter (bomb calorimeter) with the same sample for validation and evaluation of the correction factor will be still required.

CHAPTER 5

Determination of Heating Value by an Open System Calorimeter

5.1 Introduction

In this study, many indices from mass and heat balance analysis would be applied to estimate the heating value as used to find the heating value of material in boilers or furnaces system (Thumann and Mehta, 2008). A simple calorimeter from chapter 4 would be an equipment to measure energy output indices. Thumann and Mehta (2008) briefed as below:

(1) Energy input

Chemical energy was applied as the initial form and electrical energy for the igniting to a sample. For each input it is necessary to measure mass and the quantity of the electrical current for fuel and electric, respectively.

(2) Energy output

a. Energy output to a product but in this study, heat transfer to water was considered instead of energy output to a product, and this was called the gained heat output.

b. With dry flue gas, the composition, discharge rate and temperature of each outflow from the process unit.

c. Evaporation of water formed from hydrogen (H_2) in material, moisture present in material and air during the combustion.

d. From apparatus surface to the ambient environment by radiative, convective and conductive heat transfer.

e. Heat recovery from unburned material; energy should not be discarded with fuel gas exhausting to the atmosphere. But in the case of this study, energy included in the

remaining material after the process finished was pointed.

f. Other remaining unaccounted outputs were considered from above listed outputs in every part of the apparatus.

Hence, this study aimed to determine heating value for solid biomass fuel by using an open system calorimeter (OSC). OSC is easy to build and has cost-benefit performance and expected a contribution for biomass energy development. Furthermore, a relationship between measured higher heating values by OSC and commercial calorimeter or bomb calorimeter (BC) was developed.

5.2 Materials and methods

Rice straw was applied to estimate heating value by OSC and compared with commercial bomb calorimeter (BC). The heating values by OSC were analyzed by mass and heat balance methods. The steps involved in this study are listed below:

5.2.1 Sample preparation

Hino Hikari was listed as Japan's third largest cultivated varieties of rice by total area of cultivation (National Agriculture and Food Research Organization, 2010) and it was sampled to determine higher heating value (HHV) by the OSC in this study. Range of rice straw's moisture content was 6.91% to 13.55%. Rice straw was milled to less than 1.32 mm for examine in both OSC and bomb calorimeter (BC).

For the experimental data, the HHV by BC and carbon content were investigated. The HHV was determined in accordance with Standard Test Method for Gross Calorific Value of Coal and Coke (ASTM D2015) by using a Gallenkamp, Autobomb automatic adiabatic bomb calorimeter (London, UK). For carbon content, Dichromate Redox method was used to estimate.

5.2.2 Experimental apparatus

OSC which was used to study feasibility of determining the heating value accompanied with the mass and heat balances was shown schematically in Figure 5.1. OSC was 5.5 kg in total weight, built from diatomaceous earth with a hollow cylinder. The diameters were 120 and 220 mm, and the heights were 160 and 235 mm for inner and outer, layers respectively.

The first law of thermodynamics for open system was used for analysis in this study as described by Cengel and Boles (2006).

Applying law of conservation of mass to OSC process and considered in a steady state, is given by,

$$\sum M_i = \sum M_e \tag{5.1}$$

where

$$\sum M_i = M_s + M_a \tag{5.2}$$

$$\sum M_e = M_f + M_{ub} + M_{inc} + M_{cw} + M_o \tag{5.3}$$

$$M_s = M_b + M_{ub} + M_{inc} \tag{5.4}$$

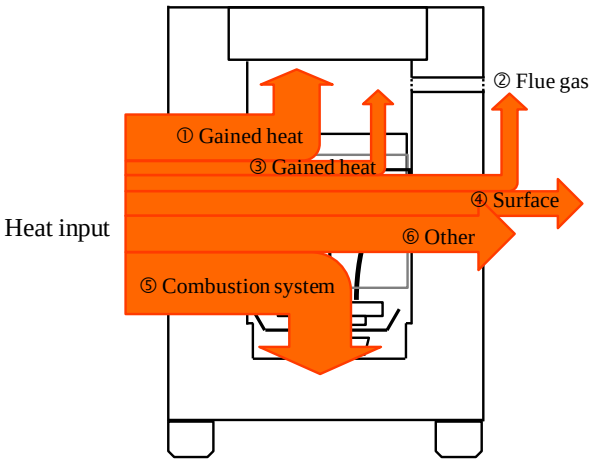


Figure 5.1. Schematic diagram of the open system calorimeter.

Applying first law of thermodynamics or heat balance, the heat coming into a system can be balanced with the heat coming out and the energy stored.

Therefore heat inputs and heat outputs were investigated. Heat inputs were estimated the heat values from electric power and heat reaction of sample. In the case of output, six of heat values were sampled, including heat output due to transfer to water (gained heat), heat of flue gas, heat output due to evaporate of water formed from hydrogen, heat output due to transfer to the surface, heat output due to unaccounted (other outputs) and heat output due to combustion which include of heat output due to incomplete combustion and unburned, to the OSC process which gives rise to

$$\sum E_i = \sum E_e + \sum E_{comb} \tag{5.5}$$

where

$$\sum E_i = E_s + E_p \tag{5.6}$$

$$\sum E_e = E_g + E_f + E_{cw} + E_{surf} + E_o \tag{5.7}$$

$$\sum E_{comb} = E_{ub} + E_{inc} \tag{5.8}$$

From Eqs. 5.5 to 5.8, the heat combustion of sample was achieved. Condensable water vapour which was produced during the combustion was carried to bottom of bowl and converted to water. Therefore, the heat combustion of sample was inferred as a higher heating value, which was determined,

$$HHV = E_s / M_s \tag{5.9}$$

The heating value from the OSC was compared with the experimental data of the heating value which was determined by bomb calorimeter (BC) in accordance with Standard Test Method for Gross Calorific Value of Coal and Coke by the Adiabatic Bomb Calorimeter (ASTM D2015).

To validate the OSC, the relative error was used to consider the satisfaction

(Channiwala et al, 2002). The relative error was considered contrast of experimental data between OSC and BC. The quantity of the relative error is defined as;

$$\%Relative\ error = \left| \frac{HHV_{BC} - HHV_{OSC}}{HHV_{BC}} \right| \times 100 \tag{5.10}$$

For the evaluation of OSC, measurement uncertainty analysis was conducted in this study at the 95 % confidence level. The measurement uncertainty analysis methodology used was recommended by the United Kingdom Accreditation Service, 2000. For present, uncertainty analysis was dealt with the terms of indirect measurement (heat output) which give strong effect to totally heat output. Other sources of uncertainty, i.e. data reduction (round off, truncation) and personal operation were ignored as this study. The expanded uncertainty was expressed as

$$\frac{u_{HHV}}{HHV} = K \frac{\sqrt{\left(\frac{\partial f}{\partial x} u_x\right)^2 + \left(\frac{\partial f}{\partial y} u_y\right)^2}}{f(x,y)} \tag{5.11}$$

For derive the relationship between measured high heating value by OSC and commercial calorimeter (bomb calorimeter), six predictors included gained heat, flue gas output, condensed output, surface output, other outputs and combustion output were consider. Multiple linear regression (MLR) method was performed in order to identify the correlations. MLR gives depth and flexibility to specify models and to choose predictor order inclusion. Backward type of regression was used. At each step of the backward type, the procedure removes the least significant predictor in the dataset. The correlation coefficient (R) was used to indicate the correlation. The square of the coefficients of determination (R^2) was mainly used for assessing adequacy for coefficients of determination of the relationship. Also, adjusted R^2 (R^2_{adj}) was used to eliminate shortcoming in a relationship as the result of the number of explanatory terms were not

suitable (Chang et al., 2007). The standard error of estimation (SEE) was considered to select the relationship as well (Huang et al., 2008). R, R^2, R^2_{adj} and SEE were calculated by SPSS statistical software. Finally, the validation of unified model was considered by contrasted the error from the calculated models with experimental data from BC.

5.3 Results and discussion

5.3.1 The determining of the higher heating value by the OSC

The processes of the determination by OSC were assumed to be under a steady state, and there were carried out on 13 samples of rice straw as solid biomass fuel. The sample weight should keep under 0.3 g. The operation time of OSC was about 30 min for a sample. At a time during operation, flow rate of air from inlet and flue gas from combustion part, temperature in each part were acquired and used to compute to heat inputs and outputs.

Table 5.1 shows the results of heat inputs and heat outputs which were computed from experimental data by OSC. The results of heat output in this study were similar to the previous study (chapter 4) where the sequences of heat output from the highest to the lowest were from 3225.0 to 5960.1 kJ/kg of the combustion output (the sum of E_{inc} and E_{ub}), 3270.0 to 5093.0 kJ/kg of the gained heat, 2137.3 to 3686.0 kJ/kg of the other outputs, 496.2 to 2122.6 kJ/kg of the surface output (the sum of E_{rad}, E_{conv} and E_{cond}), 155.9 to 305.9 kJ/kg of the condensed water output and 65.5 to 194.4 kJ/kg of the flue gas output.

Table 5.2 shows ratios of heat output in each part of OSC, HHV from OSC and BC and ratios of relative error between HHV of OSC and BC. The differences of HHV between OSC and BC varied from 13.3 to 36.7% and average was 24.4%. The high value of the relative error showed that some heat losses occurred during process.

Simple correlations between the relative error and the heat output due to gained heat, surface output, flue gas output and condensed water output were considered using plots exhibited in Figure 5.2. Correlation between relative error and the heat output due to combustion system, other outputs and electric input were considered as shown in Figure 5.3.

By checking heat loss, the reasons in each part of OSC were investigated. The relative error showed a poor correlation to the gained heat (Fig. 5.2a), the surface output (Fig. 5.2b), and the flue gas output (Fig. 5.2c) and the condensed water output (Fig. 5.2d). The heat transfer might be uniformly distributed to the water and to the wall for gained heat and surface output, thus they did not affect the error. Also, the heat output with condensed water and flue gas did not affect error, but it might be due to the fact that there was a little heat output in these parts.

Although the correlations between relative error with heat output from the combustion system and other outputs, and in case of the electric input, were not quite clear but the heat output from the combustion system and others seemed to negatively contribute to the relative error as shown in Figures 5.3a and 5.3b, respectively, while Figure 5.3c indicated the increase in the relative error with the higher electric power input in OSC's combustion system.

The above results showed that the combustion system of OSC included unaccounted heat loss and there were many characteristics that had to improve. Moreover, there might be loss of ash by the air flows through combustion chamber. As with the results of previous study, the heat output due to unaccounted values were estimated from the calibrated known values. Therefore other outputs for every examination came from the estimated value, which included all error of each apparatus.

When considering the power input to burn the sample as the ignition system, the applied electric power varies and may increase the difference of measured HHV values between OSC and BC, which might affect the operation time to ignite, thus the optimized operation time and monitoring method during ignition will be considered for next step improvement.

5.3.2 Evaluation OSC

From above mentioned, heat output due to combustion, heat output due to transfer to water and heat due to other outputs were influences on total heat output by OSC. Therefore theses parameters were considered to evaluate OSC uncertainty. The results of evaluation OSC between 14 to 16 MJ kg^{-1} by uncertainty analysis showed, standard uncertainty of combustion output was highest with 0.82% of measured value in the same way with relative error analysis. Standard uncertainties of other outputs and gained heat were 0.26% and 0.14%, respectively. OSC uncertainty was ±1.74%, the reported expanded uncertainty was based on a standard uncertainty multiplied by a coverage factor was 2, providing a level of confidence of approximately 95%. This uncertainty had quite low, OSC may make good quality measurements.

Table 5.1. Summary the results of heat inputs and heat outputs by OSC

No.	Heat input (kJ/kg)			Heat output (kJ/kg)									
	E_e	E_s	*Tot*	E_g	E_{conv}	E_{rad}	E_{cond}	E_f	E_{cw}	E_{inc}	E_{ub}	E_o	*Tot*
1	3151.1	11638.4	14789.5	4030.7	585.0	1495.8	41.8	128.6	305.9	3219.9	2327.7	2654.1	14789.5
2	2145.0	12566.8	14711.8	4452.7	336.5	880.7	26.8	172.8	235.7	4090.8	1256.7	3259.1	14711.8
3	2199.7	11250.4	13450.1	3932.4	522.2	1175.3	86.6	151.0	235.7	3954.1	562.5	2830.3	13450.1
4	1307.3	13094.3	14401.6	3270.0	349.7	917.9	27.9	168.5	196.0	4476.2	1309.4	3686.0	14401.6
5	1944.0	10287.1	12231.1	4754.9	151.4	388.5	15.5	90.8	196.0	3510.5	514.4	2609.1	12231.1
6	1668.0	12731.0	14399.0	3967.8	302.5	794.9	16.1	194.4	191.2	4836.0	636.6	3459.5	14399.0
7	2125.0	12462.4	14587.4	4062.9	302.9	815.5	36.3	136.3	155.9	5221.7	623.1	3232.8	14587.4
8	2149.7	9432.0	11581.7	4245.2	274.8	642.4	11.9	111.8	200.5	3346.3	471.6	2277.3	11581.7
9	2376.0	9210.7	11586.7	5093.0	249.2	529.8	10.7	158.1	183.6	2764.4	460.5	2137.4	11586.7
10	2604.0	10083.5	12687.5	4669.4	116.1	304.1	76.0	100.5	196.0	3878.1	1008.4	2338.9	12687.5
11	2328.5	12682.6	15011.1	4814.4	193.6	527.2	18.1	65.5	194.3	5326.0	634.1	3237.9	15011.1
12	2074.3	10107.6	12181.9	4457.7	149.1	373.5	8.9	89.3	158.4	3927.4	505.4	2512.2	12181.9
13	1779.3	10687.7	12467.0	3637.9	224.5	539.4	21.4	105.1	247.6	4371.0	534.4	2785.7	12467.0

Table 5.2. Ratios of heat output in each part of the OSC, the HHV from OSC and BC, and ratios of relative error between HHV of OSC and BC

No.	Heat output (kJ/kg)						*HHV* (MJ/kg)		*%Relative error*
	E_g	E_{surf}	E_f	E_{cw}	E_{comb}	E_o	OSC	BC	
1	27.25	14.35	0.87	2.07	37.51	17.95	11.64	14.94	22.10
2	30.27	8.46	1.17	1.60	36.35	22.15	12.57	14.65	14.24
3	29.24	13.26	1.12	1.75	33.58	21.05	9.58	15.05	36.34
4	22.71	9.00	1.17	1.36	40.17	25.59	13.09	15.11	13.34
5	38.88	4.54	0.74	1.60	32.91	21.33	12.34	14.58	15.36
6	27.56	7.73	1.35	1.33	38.01	24.02	12.73	15.09	15.64
7	27.85	7.92	0.93	1.07	40.07	22.16	12.46	14.96	16.68
8	36.65	8.02	0.97	1.73	32.96	19.67	9.43	14.64	35.56
9	43.96	6.82	1.36	1.58	27.83	18.45	9.21	14.56	36.73
10	36.80	3.91	0.79	1.54	38.51	18.45	9.72	14.88	34.67
11	32.07	4.92	0.44	1.29	39.70	21.58	12.68	15.26	16.91
12	36.59	4.36	0.73	1.30	36.39	20.63	10.11	14.50	30.27
13	29.18	6.30	0.84	1.99	39.35	22.34	10.69	14.99	28.72

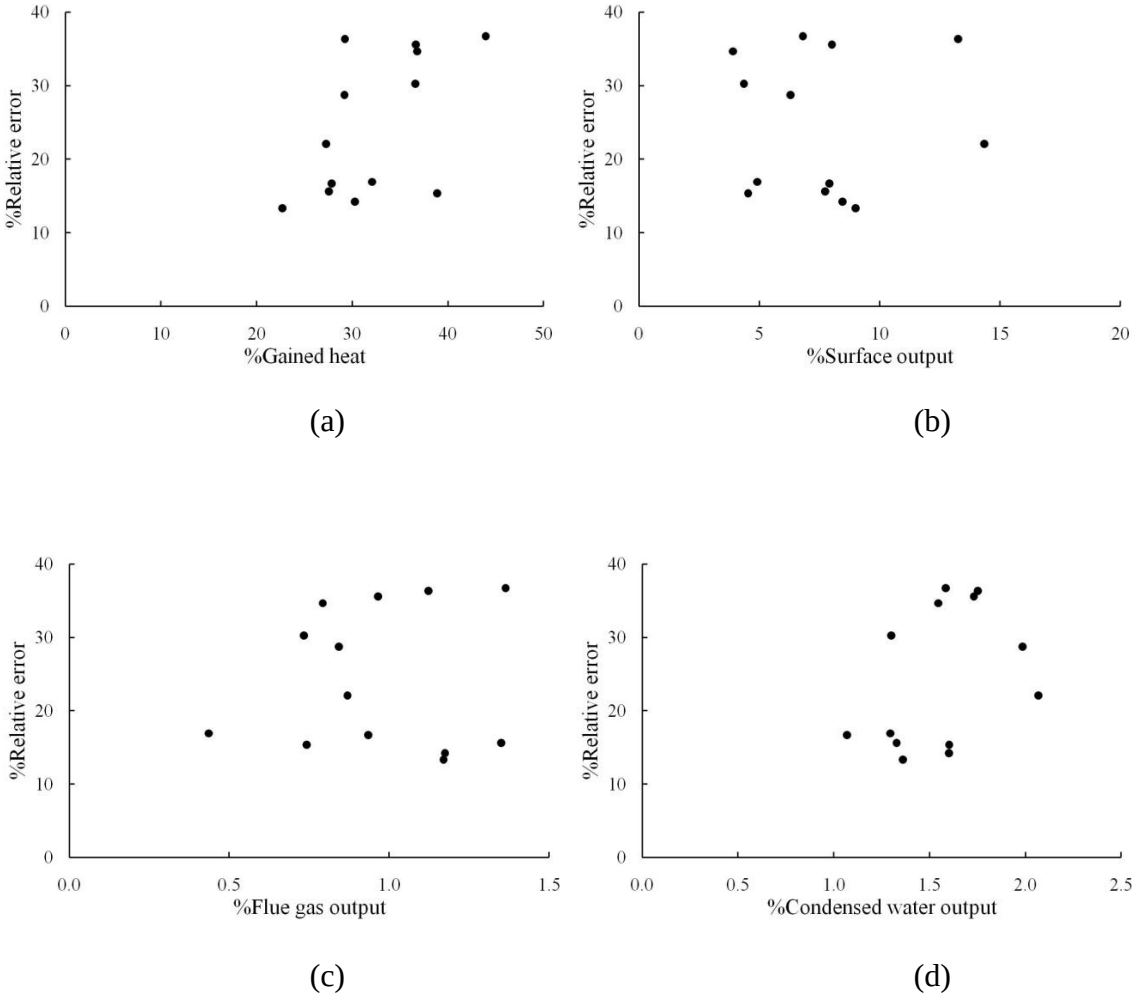
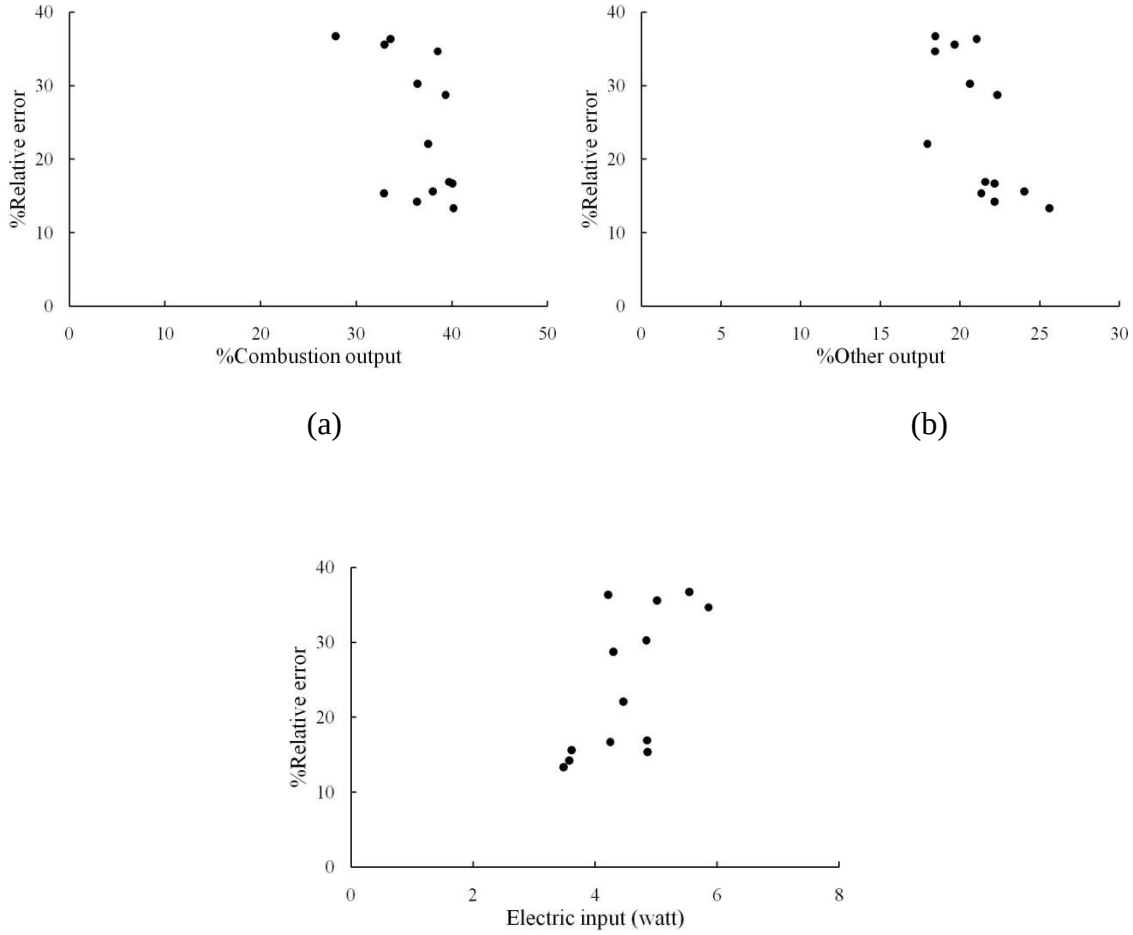


Figure 5.2. Correlation between the relative error and %gained heat (a), %surface output (b), %flue gas output (c), %condensed water output (d).



(a) (b)

(c)

Figure 5.3. Correlation between the relative error and %combustion output (a), %other outputs (b) and electric input (c).

5.4 Conclusion

To begin to develop OSC for determining the heating value, the uncertainty and relative error analysis were conducted to evaluate OSC. For relative error, there was a large error between measured HHV from OSC and BC. The various factors affecting OSC's efficiency came from combustion system, the interval of energy input and achieving other outputs. Therefore, heat loss by some leaks around the instrument should not disregard. However, uncertainty of OSC had quite low by uncertainty analysis.

CHAPTER 6

Relationships between Major Constituents, Storage Conditions, and Higher Heating Values of Rice Straw

6.1 Introduction

Heating value is one of the most important fuel properties; it defines the amount of heat released from combustion (Huang et al., 2008). Searching the optimum utilization of each conversion processes is an essential goal for most energy studies. Therefore, to determine the energy output of the conversion methods, the heating value was considered as a main factor. The heating value can be directly determined experimentally from a closed system such as the environments measured by adiabatic and isothermal calorimeters (Hsi and Kuo, 2008; Sheng and Azevedo, 2005). Another important method obtains the heating value by indirect estimation from proximate and ultimate analyses using a mathematical relationship. Table 6.1 shows summary of equations in the literature that are used to predict higher heating value (HHV) of biomass from proximate and ultimate analyses. These equations have been derived for analyzing the heating value of biomass. Equations 6.1 – 6.4 are based on ultimate analysis (carbon, hydrogen, oxygen, nitrogen, sulfur), and Eqs. 6.5 to 6.11 are based on proximate analysis (ash, volatile matter). The details are shown in Table 6.1.

Table 6.1. Summary of equations in literatures used to predict higher heating value of biomass

Eq.	Model	Basis and assumptions	Ref.
6.1	HHV = 0.4373*C* – 1.6701	This equation derives the HHV for biomass materials, and its accuracy was 5% for the entire range of biomass materials.	Channiwala and Parikh, 2002 citied from Tillman, 1978
6.2	HHV = 0.4571*C* – 2.7	This equation derives the HHV based on the percentage of carbon in the biomass when the material is dry.	Brown, 2004
6.3	HHV = 0.3259*C* + 3.4597	This equation derives the HHV for biomass materials, and R^2 was 0.758.	Sheng and Azevedo, 2005
6.4	HHV = [33.5*C* + 142.3*H* – 15.4*O* – 14.5*N*] × 10^{-2}	This equation estimates the HHV for different lignocellulosic materials or biomass fuel.	Demirbas, 1997
6.5	HHV = – 1.3765 + 0.3137*C* + 0.7009*H* + 0.03180*O*	This equation derives the HHV for biomass with a ±5% error.	Sheng and Azevedo, 2005
6.6	HHV = 0.196(*F*) + 14.119	This equation is obtained from 16 different lignocellulosic sources, and the correlation coefficient was 0.9997.	Demirbas, 1997

Table 6.1. Summary of literatures on equations to predict the higher heating value of biomass (cont.)

Eq.	Model	Basis and assumptions	Ref.
6.7	HHV = 0.3133 (100 – (*V* + *F*)) – 10.81408 or HHV = 0.3133 (100 – *A*) – 10.81408	This equation derives the HHV for all types of biomass. The different residues are considered with errors < 10%.	Jiménez and González, 1991
6.8 6.9	HHV = – 2.737 – 0.16043*M* + 0.26676*V* HHV = 18.65503 – 0.15473*M* – 0.20617*A*	These equations derive the HHV for rice straw and wheat straw with R^2 equal to 0.828 and 0.905, respectively.	Huang et al., 2008
6.10	HHV = 35.43 – 0.1835*V* – 0.3543*A*	This equation derives the HHV for lignocelluosic materials and charcoals.	Cordero et al., 2001
6.11	HHV = 19.914 – 0.2324*A*	This equation derives the HHV for biomass with R^2 equal to 0.625.	Sheng and Azevedo, 2005

Note: HHV is the higher heating value, measured in MJ/kg; *C, H, O, N, S, A, V, M,* and *F* represent the carbon, hydrogen, oxygen, nitrogen, sulfur, ash, volatile matter, moisture, and fixed carbon concentration expressed in % of the material when it is dry.

The Food and Agriculture Organization of the United Nations (1994), however, reported that storage conditions might be a factor that changes the properties of biomass materials, because biomass materials deteriorate during storage because of biological degradation processes. These results corresponded with Phayom and Tanaka (2009) who found that the storage conditions, such as storage periods (after harvesting until 6

months), storage temperatures (10°C, 20°C, and 30°C), and the size of rice straw (untreated, cut, and milled), affected the constituents of rice straw (carbon, nitrogen, moisture, and ash concentrations), because most of the rice straw suffered degradation after harvest. Especially, during the first month of storage, concentrations of the rice straw constituents would decrease rapidly. In addition, the storage temperature of 30°C showed the greatest influence to the condition of the straw. As the storage period and storage temperature increased, carbon, nitrogen, moisture, and ash concentrations decreased from 39.9% to 33.4%, 0.50% to 0.35%, 22.1% to 11.8%, and 15.1% to 14.8%, respectively.

To develop an alternative method for determining the HHV based on two reasons: (1) The concentrations of carbon, nitrogen, moisture, and ash in rice straw vary depending on storage conditions, and (2) both previously mentioned methods to determining HHV are complicated and time-consuming processes that require set-up equipment, measuring methods, and calculating procedures. To investigate the relationship between the heating value and storage conditions to discover a way to provide a rapid, easy, and convenient determination process. To ensure that we developed an appropriate model that resulted in highly accurate measurements, we used the HHV and storage conditions (storage period and temperature) to express the relationship between the proximate analysis (moisture and ash concentrations) and the ultimate analysis (carbon and nitrogen concentrations) by individually analyzing the two.

To develop relationships between the HHVs by the proximate and ultimate analyses of rice straw while examining storage conditions, an MLR was performed. MLR is a technique used to model a relationship between two or more independent variables and a dependent variable by fitting a linear equation to the observed data (Chang et al., 2007). The MLR was performed for each analysis to provide a prediction capability, and the

relationship was analyzed with the previously mentioned results in the literature to validate the most appropriate form of relationship.

6.2 Materials and methods

To determine how storage conditions affect the relationships between the basic properties and the HHV of rice straw, we carried out the following steps to develop and derive the unified relationships:

6.2.1 Sample preparation and storage conditions

The rice straw variety used in this study was Hino Hikari, which was listed as Japan's third largest cultivated variety by the total area of cultivation (National Agriculture and Food Research Organization, 2010). Two storage conditions were controlled in this study: storage period and temperature. Rice straw was stored after harvesting for 156 days from November 2009 to April 2010. Three sets of rice straw were separated and stored in three incubators at three different temperatures: 10°C, 20°C, and 30°C, respectively. In this study, the average length of an individual rice straw was 775 mm, and the density of the rice straw was 110 kg/m^3.

6.2.2 Sample analyses

Rice straw samples in every condition were examined each month by the proximate analysis (moisture and ash concentrations) and ultimate analysis (nitrogen and carbon concentrations). Nitrogen and carbon concentrations were analyzed by weight percentage by the Kjeldahl method and Dichromate Redox method, respectively. The experimental value of the HHV was determined by an adiabatic calorimeter or a bomb calorimeter in accordance with the Standard Test Method for Gross Calorific Value of Coal and Coke using the adiabatic bomb calorimeter (ASTM D2015).

6.2.3 Heating value models

For derive the HHV models, three main steps were conducted in this study. The first step aimed to study correlations of the proximate and ultimate analysis data that were individually examined for various storage conditions. The constituents that had the highest correlation were considered for the second step. The second step determined the relationships of the HHVs by the proximate and ultimate analyses that had been identified in the first step. During the last step, relationships from the first and second steps were defragmented, and relationships between major constituents, storage conditions, and the HHV of rice straw were determined. The MLR method was considered to satisfy the correlations in the first and second steps, and the new models from the third step were verified with models from the literature. The details of each step are as follows:

Step 1. Relationships between major constituents in various storage conditions

The MLR method was considered to satisfy the correlations; the conditions are as follows:

$$Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + E_p \quad (6.12)$$

where Y is a dependent variable (carbon, nitrogen, moisture, or ash concentrations), and X_1 and X_2 are independent variables. X_1 indicates the storage period, and X_2 indicates the storage temperature; E_p is an error term of the predictive model; and β_0, β_1, and β_2 are regression coefficients. The parameter β_0 is the intercept of this plane. β_1 represents the change in the mean response corresponding to a unit change in X_1 when X_2 is held constant. Similarly, β_2 represents the change in the mean response corresponding to a unit change in X_2 when X_1 is held constant.

For the adjustable parameters in each expression or the goodness of the fitting curve, the least square, minimizing the error squared methods were accompanied (Thipkhunthoda et al., 2005) with the Gauss elimination method by MATLAB software.

The square of the coefficient of determination (R^2) was mainly used for assessing the adequacy of using coefficients to determine the correlation between each proximate and ultimate analysis while also considering storage conditions. Also, adjusted R^2 (R^2_{adj}) was used to eliminate any shortcoming in a relationship that might result from the number of explanatory terms not being suitable (Chang et al., 2007). The standard error of estimate (SEE) was considered when selecting the relationship as well (Huang et al., 2008). R^2, R^2_{adj}, and SEE were calculated by SPSS (Statistical Package for the Social Sciences) statistical software.

Step 2. Relationships between HHV and concentrations of major constituents

Almost all the processes of this step were the same as those performed in the first step, except the parameters were replaced as follows:

From Eq. 6.12, the dependent variable (*Y*) was used as the HHV. Independent variables were carbon, nitrogen, moisture, and/or ash concentrations, which were identified to have a high correlation.

Step 3. Relationships between major constituents, storage conditions, and HHV

The relationships from the first and second steps were combined, and the relationships between major constituents, storage conditions, and the HHV of rice straw were attained. During this step, the validation of a unified model was considered by contrasting the error from the predicted models with experimental data and by comparing it with the models found in the literature. To verify the predicted models, we used other samples of rice straw to apply the same method part of analysis. The average bias error (ABE) was considered for satisfaction of the models. It indicates the average bias error or systematic error of a relationship (Thipkhunthoda et al., 2005; Sheng and Azevedo, 2005; Channiwala and Parikh, 2002). ABE is defined as follows:

$$\text{ABE (\%)} = \frac{1}{n}\sum_{i=0}^{n}\left(\frac{HHV_{\mathrm{p},i}\text{-}HHV_{\mathrm{m},i}}{HHV_{\mathrm{m},i}}\right)\times 100 \qquad (6.13)$$

where HHV_m and HHV_p are the higher heating values of each data point obtained from measurement and prediction, respectively. The value i is an independently drawn observation ($i = 1,\ldots,n$) and n is the number of samples. The relationship that yielded a minimum error was considered to be the best relationship.

6.3 Results and Discussion

6.3.1 Rice straw characteristics

Table 6.2 shows the minimum, maximum, mean, and standard deviation of each major constituent of rice straw in this study.

Table 6.2. Minimum, maximum, mean, and standard deviation of major constituents of rice straw

	Minimum	Maximum	Mean	Standard Deviation
Heating value	15.59	17.28	16.30	0.63
Carbon	35.58	42.68	38.50	2.79
Nitrogen	0.37	0.67	0.48	0.12
Ash	13.61	14.74	14.21	0.32
Moisture	6.25	13.55	9.41	2.73

Note: Heating value is expressed in MJ/kg; carbon, nitrogen, ash, and moisture concentrations are expressed in % of dry material.

The HHV in this study varied in the range from 15.59 to 17.28 MJ/kg. *C*, *N*, *A*, and *M* were in the ranges from approximately 35.58% to 42.68%, 0.37% to 0.67%, 13.61% to 14.74%, and 6.25% to 13.55 %, respectively, when the material was dry.

Table 6.3 shows the correlation between the higher heating value (HHV) and each of constituents: carbon concentration (*C*), nitrogen concentration (*N*), ash concentration (*A*), and moisture concentration (*M*), by Pearson correlation.

Table 6.3. Correlations among major constituents (r)

	Heating value	Carbon	Nitrogen	Ash	Moisture
Heating value	1.000				
Carbon	0.920	1.000			
Nitrogen	0.952	0.903	1.000		
Ash	0.410	0.577	0.418	1.000	
Moisture	0.958	0.852	0.947	0.209	1.000

The concentrations of the rice straw constituents deteriorated, while the storage period and storage temperature increased. These phenomena corresponded with Phayom and Tanaka (2009) and had correlations with the HHV. The correlation between *C*, *N*, and *M* concentrations seem to positively contribute to the heating value with 0.920, 0.952, and 0.958, respectively. *C* and *N* refer to the elements based on the stoichiometry to describe the combustion of any organic compound and contributed positively towards the HHV. *M* contributed positively towards the HHV too, it may be a result of the HHV depends on the assumption made on the water is condensed out of the combustion products including sensible heat and latent heat. Decreases in the concentrations of the rice straw constituents were highest during the period from the initial storage to 30 days afterwards

in every temperature condition. Only the ash concentration was slightly different in every storage condition with a low correlation (0.410). This is probably because the ash concentration only had a small influence on the heat released during rice straw combustion (Sheng and Azevedo, 2005) in this study. Therefore, carbon, nitrogen, and moisture concentrations of rice straw would be the main variables based on the high correlation with the HHV.

6.3.2 Model analysis

(1) Relationships between major constituents and storage conditions

To determine the relationships between the heating value and the major constituents of rice straw in different storage conditions, initially attempted to understand how storage conditions affected carbon and nitrogen concentrations via ultimate analysis and how they affected ash and moisture concentrations via the proximate analysis. From Table 3, the major constituent was selected that had a high correlation with the HHV and used it to predict the relationships with storage conditions using MLR. Carbon (r = 0.920), nitrogen (r = 0.952), and moisture (r = 0.958) concentrations had a high correlation and were all significant with the heating value at a 0.01 significance level. Therefore, *C*, *N*, and *M* concentrations were selected and determined the regression coefficients and coefficients of determination (R^2) at a 95% confidence level for each relationship as follows:

$$C = 41.576 - 0.044t + 0.017T$$

($R^2 = 0.88$, $R^2_{adj} = 0.86$, SEE = ±1.06) (6.14)

$$N = 0.617 - 0.002t - 0.0004T$$

($R^2 = 0.73$, $R^2_{adj} = 0.67$, SEE = ±0.07) (6.15)

$$M = 13.428 - 0.036t - 0.066T$$

(R^2 = 0.68, R^2_{adj} = 0.61, SEE = ±0.24) (6.16)

where *C*, *N*, and *M* represent the carbon, nitrogen, and moisture concentrations (%db); *t* and *T* indicate storage period (days) and temperature (°C), respectively. Using Eqs. 6.14 to 6.16, the resulting relationships tended to be similar with the results from the rice straw characteristics part. That is, the concentrations of the major constituents would decrease when the temperature or the duration of storage increased.

When assessing the adequacy of the equations, the coefficients of determination (R^2) and adjusted R^2 were determined and they were not very different. The number of explanatory terms was suitable. Equations 6.14 and 6.15 had quite good coefficients of determination, which indicated that these equations could develop good relationships, but the results of Eq. 6.16 were quite low, where R^2 of the relationships of *C*, *N*, and *M* with similar storage periods and storage temperature were 0.88, 0.73, and 0.68, respectively. Sheng and Azevedo (2005) reported that correlations between the ultimate analysis (carbon and nitrogen) and the HHV were more accurate than those based on the proximate analysis (moisture and ash), because the ultimate analysis indicated more detailed chemical composition information than the proximate analysis. Therefore, Eqs. 6.14 and 6.15 were continually used to predict the HHV.

(2) Relationships between HHV and major constituents

A regression model for predicting the higher heating value of rice straw with *C* and *N* was developed using MLR, as shown in Eq. 6.17. The carbon and nitrogen concentrations contributed positively to the HHV, similar to the results in rice straw characteristics part. Also, the resulting MLR model (shown in Eq. 6.17) was checked using R^2, $R^2_{adj,}$ and SEE. This relationship showed good performance with low SEE, high R^2, and a small difference between R^2 and R^2_{adj}.

HHV = 11713.62 + 74.34*C* + 3571.04*N*

(R^2 = 0.926, R^2_{adj} = 0.919, SEE = ±0.19) (6.17)

where HHV is the higher heating value (kJ/kg).

(3) Relationships between major constituents, storage conditions, and HHV

The relationship between HHV and the *C* and *N* concentrations of rice straw under different storage conditions was rewritten using Eqs. 6.14 and 6.15 instead of using *C* and *N* in Eq. 6.17 as follows:

HHV = 17007.89 – 9.17*t* + 0.05*T*

(R^2 = 0.801, R^2_{adj} = 0.781, SEE = ±0.310) (6.18)

The relationship was suitable with a low SEE (±0.31) and an R^2 of 0.801 (which was similar to R^2_{adj}) and provided a level of confidence of approximately 95%.

The results from the measured and predicted HHV from Eqs. 6.17 and 6.18 are presented in Figures 6.1 and 6.2, respectively. The predicted values in both equations were quite consistent with the measured HHV.

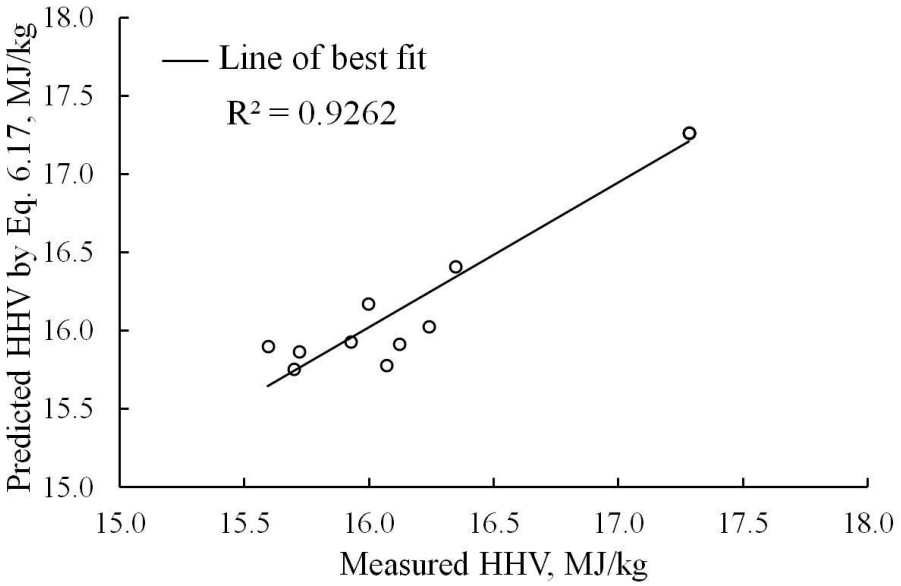


Figure 6.1. Comparison between the measured HHV and the predicted HHV using Eq. 6.17.

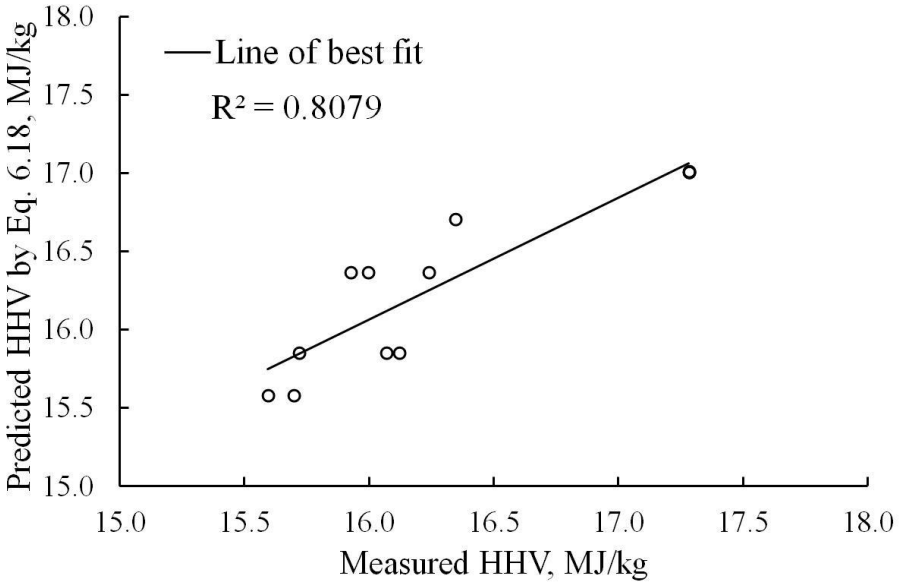


Figure 6.2. Comparison between the measured HHV and the predicted HHV using Eq. 6.18.

6.3.3 Validation of the models

Some equations from the literature were used for comparison to validate Eq. 6.17 for the relationship between the HHV with *C* and *N* and to validate Eq. 6.18 for the relationship between the HHV with *C* and *N* during different storage periods and at different storage temperatures. Equations 6.1, 6.2, and 6.3 were selected from the literatures (see Table 6.1) that were based on carbon concentration. Equations 6.1, 6.2, 6.3, 6.17, and 6.18 were confirmed by applying the calculations to the other 10 samples with the same storage conditions. For this part of the procedure, the standard deviation and the average from the samples were 1.38% and 37.21% for *C*, 0.04% and 0.50% for *N*, and 0.33% and 15.76 MJ/kg for the HHV. ABE was used for validation. Table 6.4 shows the results of the bias error or the differences between obtained values from equations and the experimental values.

Table 6.4. Results of the average bias error (ABE) between obtained values from equations with the experimental values

	Eq. 6.1	Eq. 6.2	Eq. 6.3	Eq. 6.17	Eq. 6.18
ABE (%)	7.30	9.17	1.05	−3.22	−2.05

The ABEs of Eqs. 6.1, 6.2, and 6.3 were overestimated (indicated by a positive ABE), but the ABEs of Eqs. 6.17 and 6.18 were underestimated (indicated by a negative ABE). As can be seen from these results, the predicted heating values were determined by Eqs. 6.3, 6.17, and 6.18 were slightly different in comparison with the experimental values with an ABE of 1.05%, −3.22%, and −2.05%, respectively. However, the predicted heating values were calculated by Eqs. 6.1 and 6.2 from literatures were significantly different from the experimental heating values and were much more different than the results from Eqs. 6.3, 6.17, and 6.18. The ABE values of Eqs. 6.1 and 6.2 were 7.30% and 9.17%, respectively.

6.4 Conclusion

When developing a new relationship between the heating value, carbon, nitrogen, moisture, and ash concentrations, the relationship based on carbon and nitrogen was the most accurate in this study. Therefore, the new simple relationships between the heating values and carbon and nitrogen (Eq. 6.17), and between the heating values and storage period and temperature (Eq. 6.18) were developed by linear multiple regression analysis as follows:

$$HHV = 11713.62 + 74.34C + 3571.04N \quad (6.17)$$

$$HHV = 17007.89 - 9.17t + 0.05T \quad (6.18)$$

where C and N are carbon and nitrogen concentrations (%db), t is storage period (days) and T is storage temperature (°C). The new equations produced good results with high coefficients of determination and small bias errors at a 95% confidence level. Therefore, these equations are acceptable for estimating the heating value of rice straw.

The parameters in the predicted models were derived over the entire storage period, and the decomposition of rice straw was not considered, which might have skewed the values of the parameters. However, these equations can estimate the HHV of straw at approximately 35.58%db – 42.68%db of C and 0.37%db – 0.67%db of N for a storage period that ranges from harvest to until 4 months later and a storage temperature that varies from 10°C to 30°C. Both the new equations are useful and convenient for predicting the HHV, which indicates the amount of energy available from rice straw. Eq. 6.18 is especially useful for predicting the HHV during storage, because it considers storage conditions and provides a rapid, easy, and convenient method to estimate the profitability of converting rice straw to energy.

CHAPTER 7

Influence of Storage Conditions on Rice Straw Fast Pyrolysis

7.1 Introduction

To use rice straw efficiently and practically for energy production, detailed knowledge and information of their thermal properties are required. For examples, understanding of pyrolysis behavior, pyrolysis temperature and heat requirement for pyrolysis process. These parameters are the key items in energy consumption and the occurring in pyrolysis chamber significantly determines the designing and operating parameters, energy balance analysis, and operation costs for thermal conversion process. Therefore, two systems would be suitable to use for these studies. Thermogravimetry (TG) is one of several thermal analysis methods to study pyrolysis behavior (Gani and Naruse, 2007; Stenseng et al., 2001). In a thermogravimetric system, sample mass loss is a function of temperature with very small samples. Differential scanning calorimetry (DSC) is a technique determination for heat of reaction (Stenseng et al., 2001). For determining the heat of reaction, DSC will measure heat flow as a function of temperature with total area under the curve.

Therefore, the objective of this study was to investigate influence of storage conditions on pyrolysis behavior of rice straw pyrolysis during heating process by using thermogravimetric (TG) and differential scanning calorimetry (DSC), which have been applied for analyzing pyrolysis behavior.

7.2 Experimental procedure

7.2.1 Investigation on pyrolysis stages of rice straw by using DSC and TG

Applied rice straw of 'Hino - Hikari' was harvested in the agricultural research center of Saga University, 2009. To investigate rice straw pyrolysis stages by DSC and TG's curves, thermal characteristics (mass loss and heat flow) were measured by SHIMADZU DTG-50 and DSC-50, respectively. Temperature conditions for DSC and TG were set from room temperature up to maximum temperature of 600°C, constant heat scanning rate was 10°C min^{-1} in inert atmosphere condition (20 ml min^{-1} of N_2). Sapphire ($\propto Al_2O_3$) was used as a reference material of known for calculating the specific heat. To investigate pyrolysis stages by DSC and TG's curves, the specific heat "C_p" of solid rice straw was given by Henderson et al. (1982) following equation,

$$C_p(T)=\frac{m_{\mathrm{STD}}}{m(\mathrm{T})}\frac{\left(\frac{dq}{dt}\right)}{\left(\frac{dq}{dt}\right)_{\mathrm{STD}}}C_{p,\mathrm{STD}}(T) \qquad (7.1)$$

where, C_p = specific heat, J g^{-1} °C^{-1}

m = mass, g

dq/dt = deflection (mW/mg)

T = temperature (°C)

The subscript STD indicates sapphire standard

7.2.2 Effect of storage conditions on rice straw pyrolysis

These experiments, storage conditions were storage size, storage time, and storage temperature. There were three sizes for storage size, the first one was 775 mm and named untreated straw, size of the second one was 382 mm (cut straw), and the last one was milled straw with particle size of 1.6 mm. For storage time, initial of rice straw and 4 months after harvested rice straw were conducted in these experiments. Rice straw samples were separated and stored in 4 temperature conditions; 10°C, 20°C, and 30°C

and ambient temperature (1.2°C-19.7°C, average 9.03°C). SHIMADZU DTG-50 and DSC-50 were used and temperature conditions and heat scanning rate in pyrolysis chamber were set as previous part. Heat requirement for heating rice straw and reaction were determined by integrating the above DSC curve (He et al., 2006).

7.3 Results and discussion

7.3.1 Pyrolysis stages of rice straw

Figures 7.1 and 7.2 indicated pyrolysis behavior considered from TG and DSC's curves, respectively. It indicated that rice straw on pyrolysis could be recognized into four stages followed pyrolysis temperature, 1) room temperature to 120°C, 2) 120°C to 250°C, 3) 250°C to 430°C and 4) temperature above 430°C. Table 7.1 shows the ranging temperature and named of rice straw pyrolysis stages, mass loss, and maximum heat flow rate.

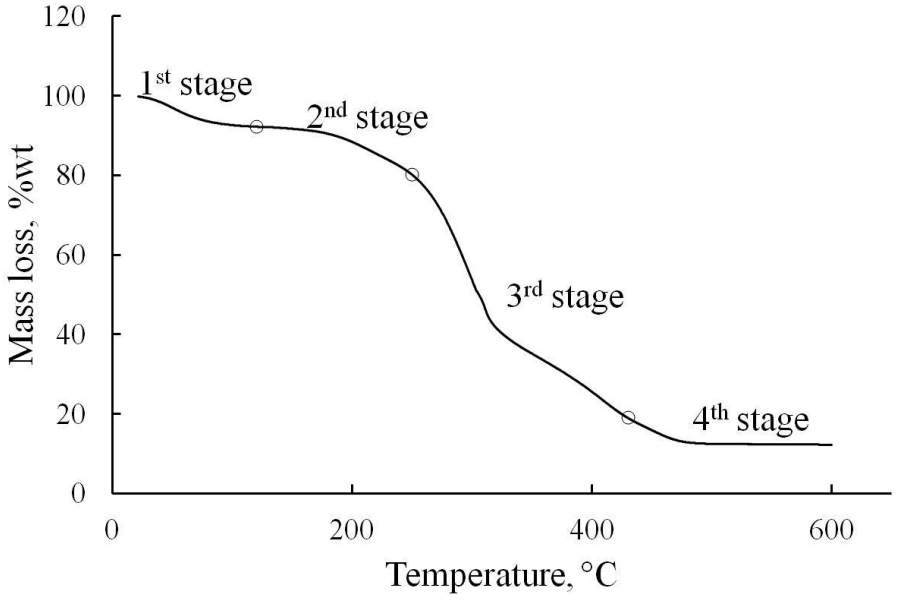


Figure 7.1. TG's curve or mass loss curve of rice straw on pyrolysis.

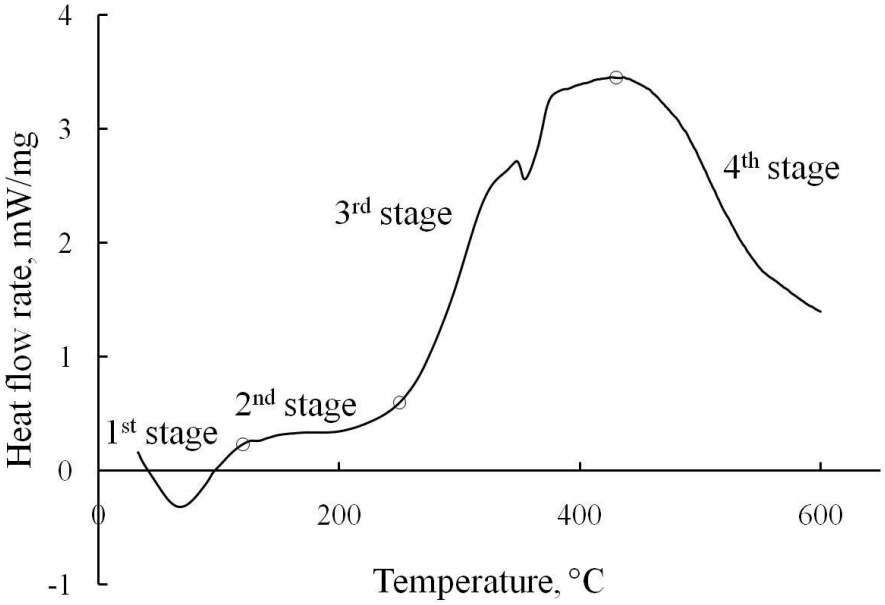


Figure 7.2. DSC's curve or heat flow rate curve of rice straw on pyrolysis.

Table 7.1. The ranging temperature and named of rice straw pyrolysis stages, mass loss, and maximum heat flow rate

Stage No.	temperature,°C	Pyrolysis stage	Mass loss, %wt	Max. heat flow rate, mW/mg
1st	Room Temp. to 120	Drying	7.56	0.23
2nd	120 – 250	Heating	12.05	0.60
3rd	250 – 430	Degradation	61.15	3.70
4th	> 430	Heating and aggregation of char	6.80	3.45

In the first stage, it showed moisture evaporation phase, as 'Drying'. This stage had a little difference of mass loss and heat flow, and it was not unstable because of the moisture influences. Therefore, in case of estimation on heat flow of the first stage, it was considered as the equal value at 120°C. In the second stage, it was for heating

sample from 0.23 to 0.60 mW/mg of heat flow. This stage, hemicelluloses started its decomposition (Yang et al., 2007) with mass loss took place from 92%wt to 80%wt (difference was 12%wt). In the third stage, 'Degradation' occurred with highest of mass loss and heat flow rate became maximum with temperature range of 250°C to 430°C. The mass loss rapidly decreased from 80%wt to 19%wt (difference was 61%wt) and maximum heat flow rate with 3.7 mW/mg. Degradation stage had 2 peaks which overlapped between decomposition of cellulose and lignin. The first peak occurred decomposition of cellulose (300°C to 350°C) with decreased mass loss was from 54%wt to 35%wt. The second peak of the third stage was attributable to decomposition of lignin which continued to the fourth stage (280°C to 450°C) with 68%wt to 13%wt of the decreased mass loss. In the fourth stage, it was for heating and aggregation of char and its mass loss was lowest changing (19%wt to 13%wt).

From mass loss curves (Fig. 7.1), temperature requirement to decomposition rice straw and produce pyrolysis gas was judged from constant mass loss. At temperature which was more than 450 ºC, mass loss would approach constant value, when temperature was more than 500ºC whole mass loss would be constant value. That means, more than 500ºC, volatile matter of rice straw was decomposed and there was only ash which will not volatilize and contributed to char yield. Therefore, ideal temperature range for bio-gas production for rice straw pyrolysis would be about 470°C to 500ºC. However, in the case of fast pyrolysis, heating rate will be higher than TG and DSC experiments (more than 100ºC/s) which accelerate the thermal decomposition (The Japan institute of energy, 2008).

The specific heat of solid phase of rice straw was determined by Eq. 7.1 accompanied with TG and DSC curves. To determine the specific heat, the influence of the moisture

and the unstable stage on the first stage was eliminated. The specific heat of rice straw was considered to be constant below 120°C by extend the value of the DSC curve after drying (at 120°C) to the beginning of the experiment. The specific heat was derived until the end of the 2nd stage (250°C) which rice straw was not in the degradation stage. In drying process for storage rice straw, it is desirable to know the specific heat. Table 7.2 shows model of specific heat of rice straw. As the results, the specific heat depend on temperature, it increased with increasing of temperature.

Table 7.2. Model of specific heat of rice straw

Temperature range (°C)	Model	R^2
Ambient temperature to 120°C	C_p=1.30	
120°C < T < 250°C	C_p=4.2715-0.0396T+0.0001T^2	0.937

7.3.2 Influence of storage conditions on rice straw pyrolysis

From previous part, four stages of rice straw pyrolysis were recognized. The objective of these experiments was to study influence of storage conditions (storage size, storage time, and storage temperature) on rice straw pyrolysis.

Figures 7.3 to 7.5 show mass loss rate, differential heat at different temperature or heat flow rate and specific heat in each rice straw pyrolysis stages, respectively. Mass loss rate, heat flow rate and specific heat were highest on degradation stage and they were the same in a previous part. Furthermore, these results showed, all of long storage time became higher of heat flow rate and specific heat than of initial condition at degradation stage. Specifically, after long storage time, the ambient temperature indicated higher heat flow rate and specific heat than these of other conditions. The straw on 10°C, 20°C

and 30°C storage conditions at 4 months after harvesting were little difference each other and there were not big difference with initial condition in case of specific heat, about 25 kJ/kg °C.

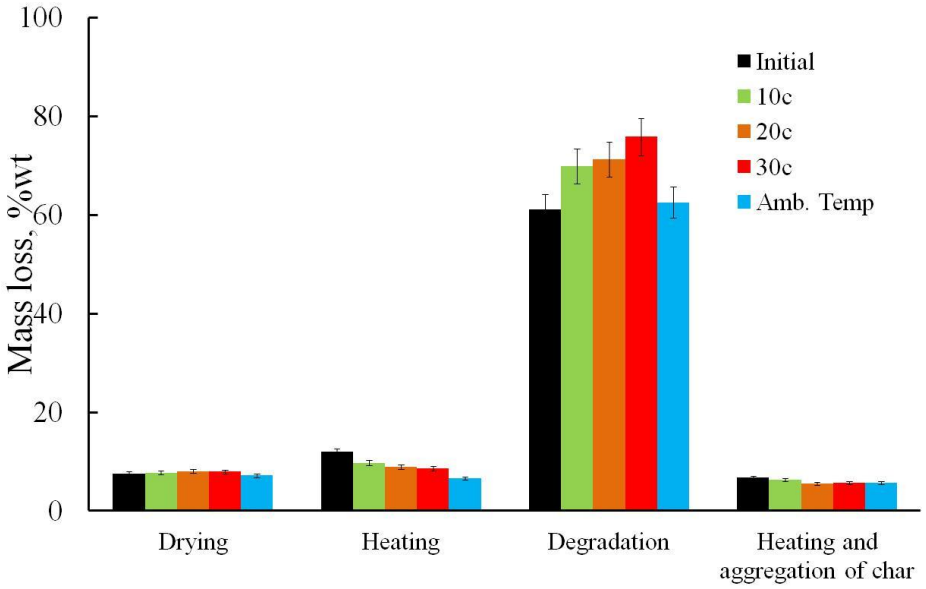


Figure 7.3. Mass loss on rice straw pyrolysis stages.

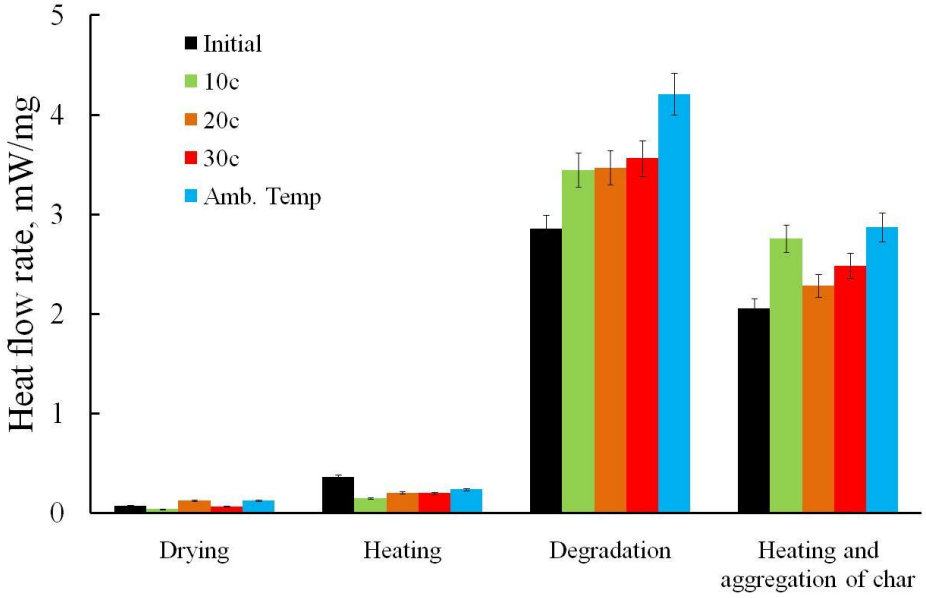


Figure 7.4. Heat flow rate on rice straw pyrolysis stages.

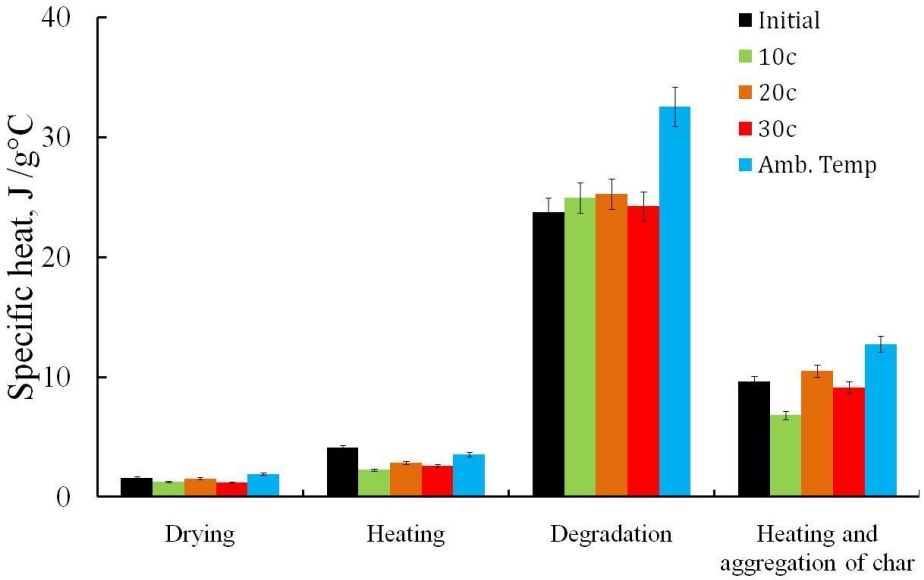


Figure 7.5. Specific heat on rice straw pyrolysis stages.

As ash concentration from ash experiment (chapter 3) was considered in this part, it can indicate to char yield. Changes of fraction of ash, mass loss, and heat requirement of rice straw pyrolysis during storage for different temperature of rice straw, 10°C, 20°C, 30°C, and ambient temperature comparing with the initial condition are shown in Figures 7.6 and 7.7.

There was difference in amount of ash between initial rice straw and 4 months stored rice straw but a bit difference on amount of ash in each storage temperature when consider only 4 months stored rice straw. Also, the mass loss in rice straw pyrolysis enables indicates to char yield in rice straw pyrolysis. However, amount of char yield when consider from TG curve was less than char yield from ash experiment. Due to the final temperature of ash experiment was 450°C while char yield would be constant at 470°C to 500°C (from previous part) as the same reason with mentioned above.

Focusing on pattern of the storage time, it affected to profile of mass loss and heat requirement. Trend of the mass loss was the highest for initial rice straw differed from

that for the others which correspond with ash experiment. Mass loss of rice straw which stored at ambient temperature was the second but highest heat requirement to decompose which similar trend with stored rice straw at low temperature (10°C). While, decomposition rate of the higher temperature conditions (more than 20°C) became lower than that of the lower temperature condition. Although, there was higher mass loss at 30°C than low temperature conditions, but there was lower heat requirement. These results suggest that the volatilization and heat requirement behavior of rice straw depends on its own storage temperature.

The results showed that 862 kJ were required to increase the temperature of 1 kg of initial rice straw from room temperature to 600°C, and 1027 kJ, 1042 kJ, 970 kJ and 1137 kJ were required for rice straw which stored 4 months at 10°C, 20°C, 30°C, and ambient temperature, respectively.

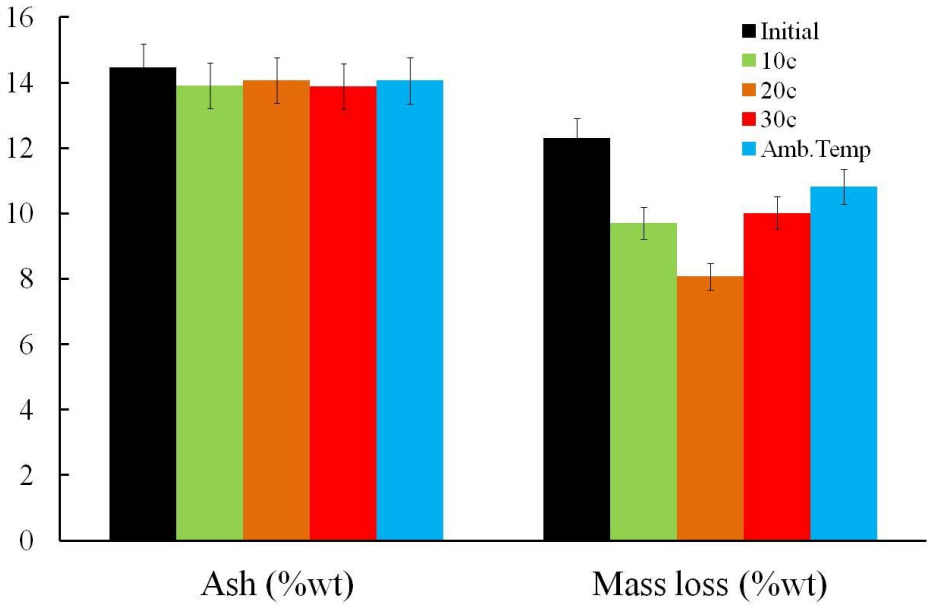


Figure 7.6. Comparison of Ash and mass loss in different storage times and storage temperatures.

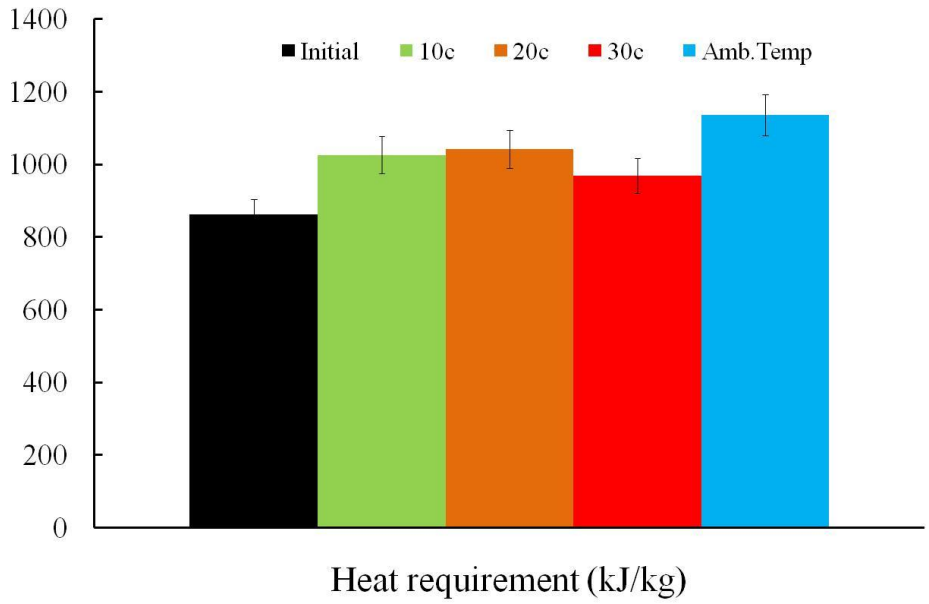


Figure 7.7. Heat requirement in different storage times and storage temperatures.

7.4 Small scale fast pyrolysis reactor

Fast pyrolysis reactor was made as laboratory scale (Fig. 7.8) for introducing pyrolysis technology. Fast pyrolysis reactor had 3 main parts, consists of pyrolysis reactor, char collector, and condensed parts. Figure 7.9 shows a schematic diagram of the fast pyrolysis apparatus. The reactor was made from SUS 304 stainless-steel pipe with an internal diameter and height of 25 and 400 mm, respectively. The main reactor was heated using ribbon heater that adjusted at approximately 500°C. Thus, the temperature of the experimental system was 450°C – 500°C. Ribbon heater was used to avoid vapor condensation until top part of char collector. Carrier gas was pure Nitrogen. The gas was injected at the top of the reactor with a flow rate of 6 – 8 L/min. Rice straw sample was ground and screened below 1 mm. The sample contained 9.0 % of moisture and 12.86 MJ/kg of higher heating value. The sample particles were fed at the top of the reactor by screw transport. The residence time inside the reaction zone was below 3

seconds. The condensable pyrolysis gas was collected in a series of condensers and cooled to a temperature of –20°C with ethanol as the cooling solvent.

Figure 7.8. Laboratory scale of fast pyrolysis reactor was used in this study.

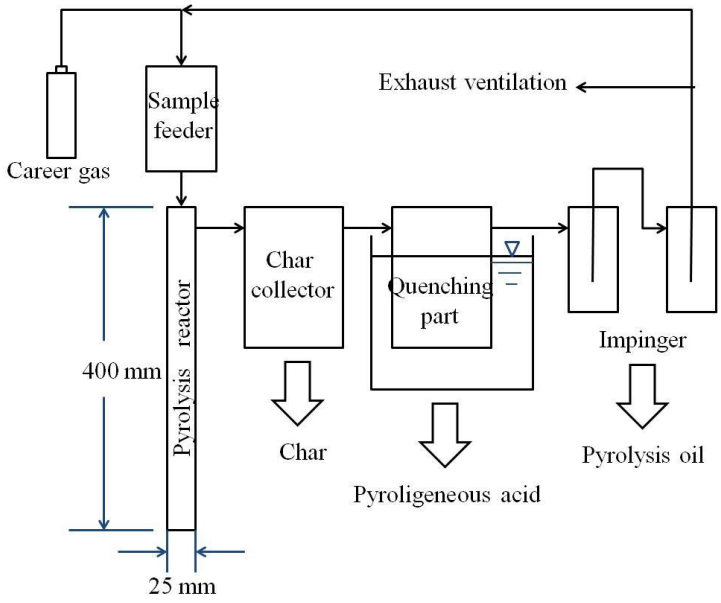


Figure 7.9. Schematic diagram of the fast pyrolysis apparatus.

After a fast pyrolysis test, most of the char was left in the collector with the yield of 30wt%. Pyrolysis gas was condensed and consisted mainly of two kinds of liquid fractions with a distinctive smoky smell. The first fraction was low viscosity and pH, heating value was as well as water due to water might be the main constituent, thus it might be pyroligneous acid (The Food and Agriculture Organization of the United Nations (FAO), 1985). The other fraction had high viscosity and density, included heavy component as tar which could burn, thus it was pyrolysis oil. In the attempt to increase the pyrolysis oil of experiments, analysis of the product evolutions at other heating conditions and improve the gas quenching and condense parts could have been worth considering. Besides, the observation of pyrolysis products by using gas chromatography-mass spectrometry could have provided even more insight into the study.

7.5 Conclusion

From results of this study, pyrolysis stage of rice straw was separated to four stages. The rice straw had highest amount of heat to raise the temperature based on a specific dry weight in the 3rd stage, namely the degradation stage of pyrolysis process. Degradation stage was an important stage, in which highest heat flow rate and highest specific heat occurred.

The models of specific heat (C_p) for rice straw before degradation were simulated. The first one is a constant value (C_p=1.30 kJ/kg°C) and available with temperature less than 120°C, the second one was derived and given by C_p=4.2715-0.0396T+0.0001T^2. This model applied with temperature range of 120°C to 250°C.

Ideal pyrolysis temperature range for bio-gas production was from 120ºC and would completely finish around 470°C to 500ºC. Storage conditions related to mass loss and

heat requirement. For storage time, in all of long storage time condition, mass loss became smaller, but higher heat requirement than initial condition. Heat requirement to increase the temperature of 1 kg of rice straw from room temperature to 600°C, for initial rice straw was 862 kJ. For storage temperature after stored 4 months, minimum and maximum heat requirements occurred at 20°C and ambient temperature, respectively. Furthermore, cut straw was the lowest of mass loss and heat requirement with 963 kJ/kg were required to increase the temperature from room temperature to 600°C.

CHAPTER 8

General Discussions

The present thesis adds insight into the field of developing biomass on multifunctional usages. Along this work, new cultivation method for rice using digested slurry produced from biogas plant instead of using chemical fertilizers, thermal behavior of rice straw representative of farm residues, and usages for rice straw as bio-fuel were studied.

The starting point for development on multifunctional usages for rice straw as biomass resource performed in this thesis was development new cultivation method for rice using digested slurry produced from biogas plant instead of using chemical fertilizers. The results from the controlled pot cultivation tests indicate that growth durations, yields, and N uptake of farmlands undergoing periodic application of digested slurry (PDS) were higher than those of farmlands undergoing one-time application of digested slurry (1DS) and applied chemical fertilizer (CF), except before the panicle initial stage (42 DAT). This result is in agreement with the report by Sasahara and Itoh (1989) in which split application of commercial compound fertilizer (at the time of plowing and/or puddling, at approximately 1 week after transplantation, at the late maximum tillering stage, and at the grain filling stage) as a rice cultivation fertilizer greatly improved the growth durations of the rice plants and increased grain yields. The reasons for these may be that CF applied as a basal dressing was mixed well in all the soil layers, whereas application of digested slurry (DS) was applied as a topdressing; plant absorption of the fertilizer applied as a basal dressing was faster than that applied as a topdressing. When consider the results between PDS and 1DS, the volume of split fertilizer applied was low; therefore, plants could absorb it rapidly. However, when a large volume of fertilizer was applied at one

time, absorption took longer. This phenomenon may occur during nitrification. As in the reports of Russo (1996) and Bijay-Singh et al. (1991), the split application of N in rice fields appeared to prevent or reduce nitrification. In addition, more N was lost via leaching during one-time application of N fertilizer after transplantation, than in split application because rice roots exhibit a limited ability to absorb and assimilate nutrients at transplantation (Bijay-Singh et al., 1991).

The reasons as mentioned previously related to physiological efficiency (PE), PE is the relationship between the yield and N uptake at panicle initiation (yield per unit N uptake) that indicates a plant's ability to redistribute N from the root to panicle at the grain filling stage (Jiang et al., 2004, Ohnishi et al., 1999). Thus, PE in this study indicated that 1DS resulted in a higher ability for assimilating N into panicles in the grain filling stage than others with the same N proportion. Because the stem number and plant height at the panicle initial stage in 1DS plants were lower than those in CF and PDS plants, the plant size of 1DS was the smallest. Although the amount of N fertilizer applied for the grain filling stage in each pot was the same, the rice plants in 1DS must have used more N fertilizer than those in CF and PDS. Phenomena of Fertilizer N-recovery efficiency (RE) were similar to N uptake. These results indicated that rice plants absorbed N fertilizer faster by PDS than by 1DS and CF, as mentioned previously. Furthermore, plant absorption of applied CF was faster than that of applied 1DS. These results may be because soil was mixed well in all layers during the application of the fertilizer as a basal dressing for CF, and thus, the root section may have had an opportunity to absorb the N fertilizer better than 1DS plants, where the fertilizer may only be in the top layers. Agronomic efficiency (AE) corresponds with total economic output or yield to the economic input or applied fertilizer during cultivation (Yadav, 2003). Yield corresponds with N uptake, and thus PDS, in which the RE was highest, had a higher AE than 1DS

and CF.

Growth durations in the actual wet rice field tests were similar to those in the controlled pot cultivation tests. PDS plots had poor results at the tillering stage but progressed in the next stages. The reasons for this were similar to the previously mentioned methods of fertilizer application. The different results of the controls between the controlled pot (D-pot) and the actual field (CF) experiments may be an effect from the previous soil in the rice field, which affected nutrient concentration. Furthermore, the results for N uptake were also similar to the first experiment. This experiment confirmed that the reason for these results was that the fertilizer applied as a basal dressing was mixed well, and thus, plant absorptions of the applied fertilizer were faster than with fertilizer applied as a topdressing. Also, periodic application of fertilizer as a topdressing decreased the occurrence of nitrification (Russo, 1996; Bijay-Singh et al., 1991).

The second main objective of this study was to study the characteristics of rice straw and develop usages for rice straw as bio-fuel. Along this work, the higher heating value (HHV) was estimated based on the energy output from open system calorimetric and based on major constituents and storage conditions, compared with measured HHV by the standard calorimetric (bomb calorimeter, BC), and thermal behavior and influences of storage conditions on the fast pyrolysis of rice straw was studied.

The energy output from the combustion parts (the unburned and the incomplete combustion) of open system calorimetric (OSC) was the highest in the results of mass and energy balances, the energy content could be better estimated by investigating remaining carbon content of material. Also, the energy outputs due to heat transfer to water, surface, condensed water and flue gas could be estimated from the above equations. But achieving of the unaccounted energy output was different from other parts. The value of

the unaccounted energy output was achieved by estimated from the calibrated known values thus it became an estimated value, not individual measured. Therefore the highest error of the determining by this method may occur from the unaccounted energy output. Furthermore, to evaluate OSC uncertainty, the uncertainty had quite low. OSC may make good quality measurements. For developing a relationship between measured HHV by OSC and BC, the backward multiple linear regressions were used to develop a relationship. This method would remove the least significant predictors in the dataset. Thus the model was defined in three parameters finally, includes combustion output, surface output and gained heat, was derived as,

$$HHV_P = 14.258 + 0.188E_c + 0.026E_{surf} - 0.081E_g \quad (8.1)$$

where, HHV_P is predicted higher heating value (MJ/kg), E_c, E_{surf}, and E_g are energy output (MJ/kg) from combustion output, surface output, and gained heat, respectively. At a 95% confidence level, the correlation coefficient of the model (r) was 0.769, the coefficient of determination (R^2) and the adjusted coefficient of multiple determination (R^2_{adj}) were similar with 0.591 and 0.538 it implies that the model is suitable for the HHV prediction. The model optimized for predicting heating value of straw presented a lower standard error of estimate ±0.183 MJ/kg. Correlation between predicted HHV and measured HHV by BC was showed in Figure 8.1, and Table 8.1 shows details of this experiment and difference between predicted HHV and measured HHV by BC (Error).

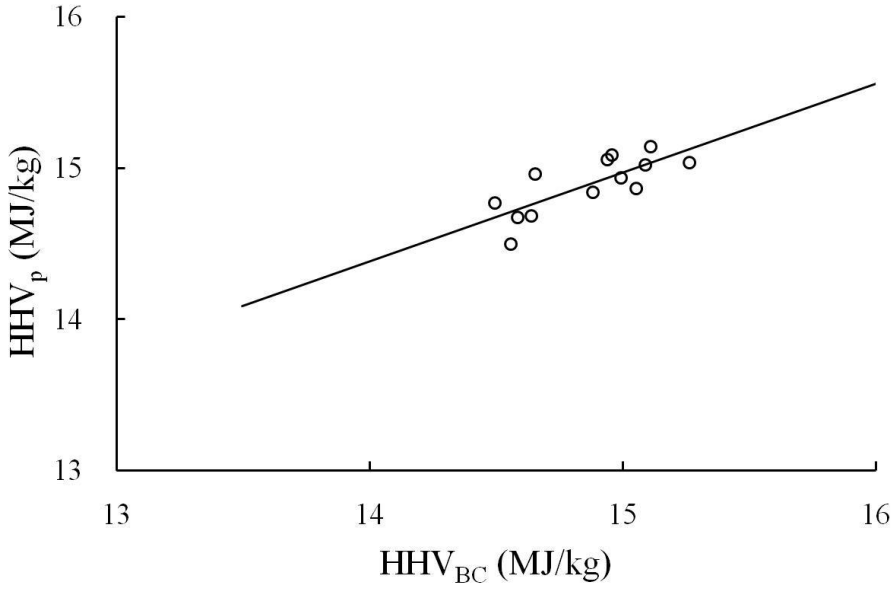


Figure 8.1. Correlation between predicted HHV and measured HHV by BC.

However, using OSC as an instrument to estimate the heating value, what we are emphasizing on improving and developing is listed below:

(1) Improving the construction of OSC for decreasing the sum of unknown heat loss.

(2) Improving the construction of combustion system to decrease the amount ash lost.

(3) Optimizing minimum ignition time in order to making superior combustion conditions.

(4) For solving the achieving of other outputs, OSC should compare and estimate with the standard values measured by BC, and then construct the calibrating methods for OSC measured values.

(5) Develop a relationship between HHV which estimated by indirect measurements (heat output sources) of OSC and HHV by BC.

Table 8.1. Details of this experiment and difference between predicted HHV and measured HHV by BC (Error)

Heat output from OSC (MJ/kg)			*HHV* (MJ/kg)		*Error*
E_c	E_s	E_g	BC	Model	(%)
5.55	2.12	4.03	14.94	15.06	– 1.30003
5.35	1.24	4.45	14.65	14.96	– 0.66334
4.52	1.78	3.93	15.05	14.86	0.00954
5.79	1.30	3.27	15.11	15.14	– 1.87107
4.02	0.56	4.75	14.58	14.67	1.294759
5.47	1.11	3.97	15.09	15.02	– 1.06288
5.84	1.15	4.06	14.96	15.08	– 1.48911
3.82	0.93	4.25	14.64	14.68	1.213459
3.22	0.79	5.09	14.56	14.50	2.44978
4.89	0.50	4.67	14.88	14.84	0.16882
5.96	0.74	4.81	15.26	15.03	– 1.15276
4.43	0.53	4.46	14.50	14.77	0.621099
4.91	0.79	3.64	14.99	14.93	– 0.46784

For the predicted heating values from major constituents and storage conditions (Eqs 17 and 18, respectively), their average bias error (ABE) were lower than ABE of Eqs. 6.1 and 6.2 from literature (Chapter 6), but similar with ABE of Eq. 6.3. This might be due to the fact that the models from this study using Eqs. 6.17 and 6.18 were developed for rice straw, which was a particular biomass material, while Eqs. 6.1 and 6.2 from the literature were developed to span all types of biomass material. Also, Eqs. 6.1 and 6.2

were based on carbon concentrations, while the new equations were developed based on carbon, and nitrogen concentrations, storage period, and storage temperature, which are probably why an increase in the accuracy were observed for the new equations. Although Eq. 6.3 was based on carbon concentration in the same way as Eqs. 6.1 and 6.2, it was derived from 200 biomass samples. Therefore, it was highly accurate (0.758) and also exhibits a slight difference in the absolute error when compared with the new equations.

For thermal behavior and influences of storage conditions on the fast pyrolysis of rice straw, results of the ash experiment from chapter 3 indicate to char yield accompanied with results of TG curve and DSC curve from chapter 7. Figures 8.2 and 8.3 show profiles of fraction of the ash, mass decrease of pyrolysis or residual mass loss, and heat requirement to decompose sample and heat reaction in different storage size of rice straw, untreated straw, cut straw, and milled straw. The vertical axis represented fraction by weight of ash and residual mass loss and amount of heat to decompose sample and react.

Trend of char yields from ash experiment had a bit difference but char yield from TG curve differed from each others. The results showed there may be a correlation with characteristics of cellulose, hemicelluloses, and lignin. General, lignin will be difficult to decompose and its reaction occur at higher temperature than cellulose and hemicellulose because lignin consists of benzene rings (Gani and Naruse. 2007; Yang et al., 2007). Therefore volatile matter of rice straw from TG experiment which was heated at higher temperature than ash experiment might be eliminated all, the char yield was lower and various more than the char yield from ash experiment. Furthermore, residual mass loss and heat requirement of cut straw were the lowest of all of the other sizes. The results showed that 1037 kJ, 963 kJ, and 1132 kJ were required to increase

the temperature of 1 kg of untreated straw, cut straw and milled straw from room temperature to 600°C, respectively.

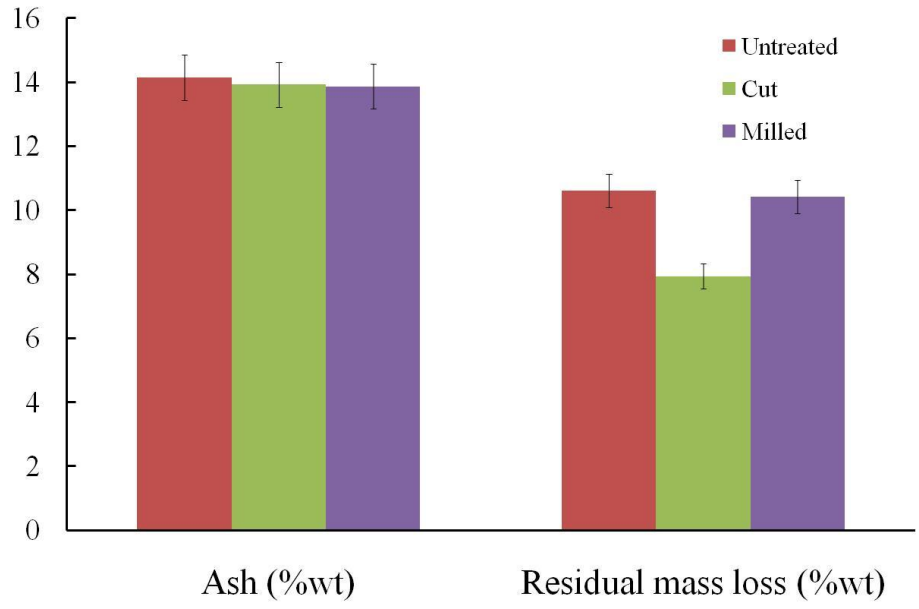


Figure 8.2. Comparison of Ash and residual mass loss in different storage size.

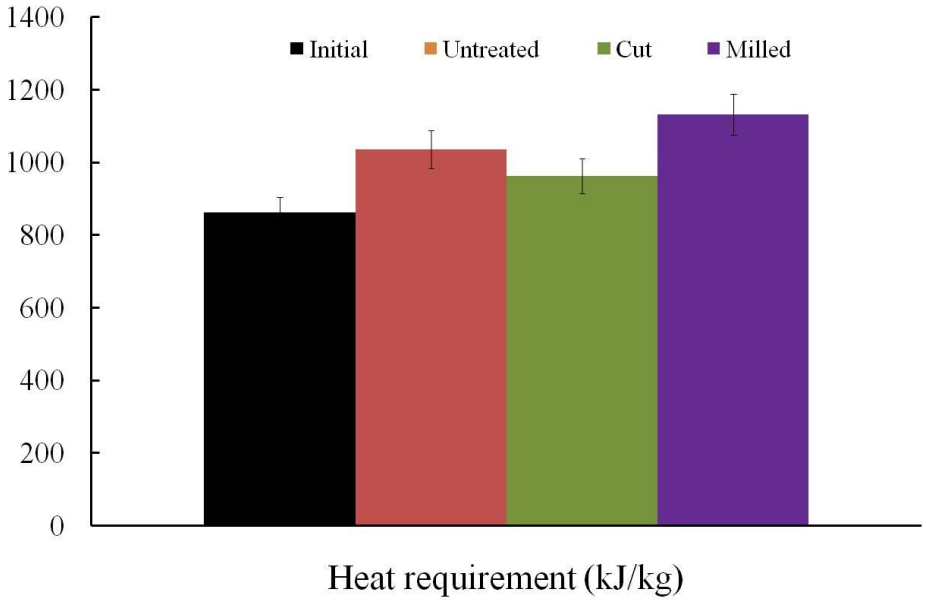


Figure 8.3. Heat requirements in different storage size.

The objectives of this study aimed to develop biomass on multifunctional usages and emphasized to rice plants. Due to grain production can be applied to be food. Besides, by-product from field or waste biomass include rice husk, rice straw, and rice bran can converted to energy. However, rice husk and rice bran are valuable nowadays, only rice straw is worthless. Thus, cycle of biomass energy conversion is simulated by using information from this study and considered only rice straw in case of by-product.

Every year 20 million tons of food waste is produced in Japan (Japan for Sustainability, 2004). If, all of food waste are fermented and transferred to digested slurry by the methane fermentation method for use in rice fields and fertilizer application rate is 120 kgN/ha with TN is 2000 mg/l. Rice fields have around 200000 ha of digested slurry applied to them, which accounts for 11.9% of the total area of rice fields (1.68 million hectares, International Rice Research Institute, 2010) in Japan. Therefore, amount of using nitrogen (supplied area × fertilizer application rate) is approximately 24,000 tons. Simulation of decreasing energy consumption and energy generation from using digested slurry and chemical fertilizer in rice fields is shown in Figure 8.4.

Using DS would reduce energy consumption from using fossil fuels for producing chemical fertilizer, approximately 1.67×10^{15} Joules. Energy generation from rice straw to pyrolysis oil are approximately 11.70×10^{15}, 10.71×10^{15}, and 11.61×10^{15} Joules for PDS, 1DS, and CF, respectively. Using DS would decrease energy and generate energy, higher gain energy than CF accounts for 15.16 and 6.63% for PDS and 1DS, respectively. However, this simulation does not include energy producing pyrolysis oil and energy from char yield in pyrolysis process.

If, 11.9% of rice fields are supplied DS as periodic application and 88.1% of rice fields are original cultivation area, we can achieve rice straw pyrolysis oil, approximately 11.70

$\times 10^{15}$ and 86.23 $\times 10^{15}$ Joules from supplied DS and original cultivation area, respectively. Therefore, total energy is approximately 97.93 $\times 10^{15}$ Joules or 2.34 Mega tons of oil equivalent (the amount of energy released by burning one ton of crude oil, Mtoe), and accounting for 0.61% of net import energy per year in Japan (Net import energy in Japan is 384.46 Mtoe, International Energy Agency, 2011).

In case of Thailand, 14.63 million tons of waste was produced in 2006 (Institute of Data and Information Services, 2009) and approximately 64% of waste was organic waste (Pollution control department, 2012), and animal waste was approximately 20.95 million tons in 2000 (Department of Alternative Energy Development and Efficiency, 2007). If, all of organic waste and animal waste are fermented and transferred to digested slurry by the methane fermentation method for use in rice fields in the same fertilizer application rate with case of Japan. Digest slurry can be applied in rice fields, approximately around 303,100 ha, which accounts for 2.8% of the total area of rice fields (11 million hectares, International Rice Research Institute, 2010). Amount of using nitrogen (supplied area $\times$ fertilizer application rate) is approximately 36400 tons. Therefore, using DS would reduce energy consumption from using fossil fuels for producing chemical fertilizer, approximately 2.53 $\times 10^{15}$ Joules. Energy generation from rice straw to pyrolysis oil are approximately 11.79 $\times 10^{15}$, 16.17 $\times 10^{15}$, and 17.66 $\times 10^{15}$ Joules for PDS, 1DS, and CF, respectively. We could conclude that, using DS would decrease energy and generate energy, higher gain energy than CF accounts for 15.07 and 5.89% for PDS and 1DS, respectively (Fig. 8.4). If, 2.8% of rice fields are periodic application of DS and other fields are original cultivation area (CF), we can achieve rice straw pyrolysis oil, approximately 17.79 $\times 10^{15}$ and 611.55 $\times 10^{15}$ Joules from periodic application of DS and original cultivation area, respectively. Therefore, total energy is approximately 629.34 $\times$

10^{15} Joules or 15.03 Mtoe, and accounting for 34.66% of net import energy per year in Thailand (Net import energy is 43.37 Mtoe, International Energy Agency, 2011).

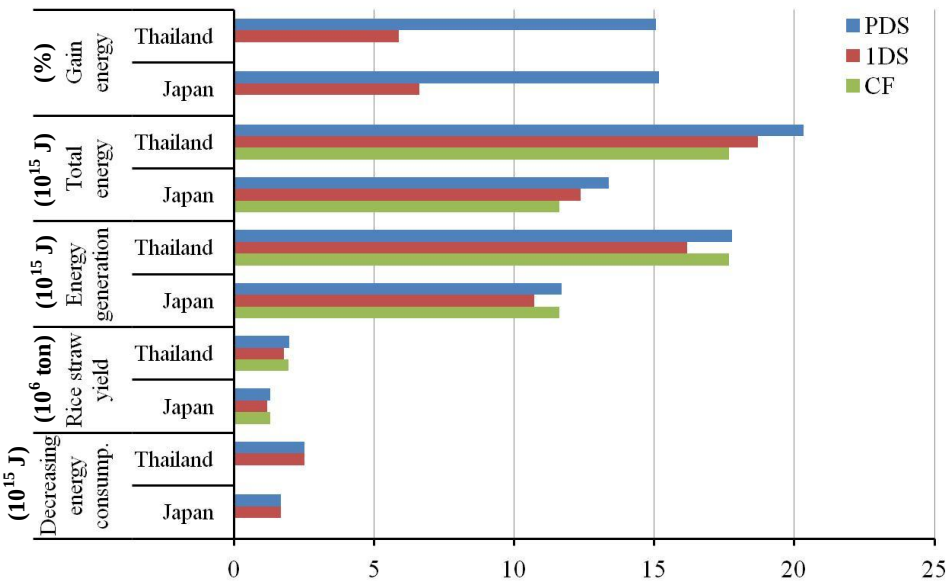


Figure 8.4. Simulation of decreasing energy consumption and energy generation in case of Thailand and Japan.

Note: Decreasing energy consumption = Amount of using nitrogen (kg)× Energy consumed of nitrogen fertilizer; Energy consumed of nitrogen fertilizer = 69.5 MJ/kg (Fadare, 2009);

Rice straw yield = (1 – HI fraction from Table 2.3) × biomass yield from Table 2.3 × supplied area;

Energy generation = Rice straw yield × pyrolysis oil fraction × Heating value of pyrolysis oil from chapter 7 (12.86 MJ/kg); Pyrolysis oil fraction = 0.7 (The Japan institute of energy (JIE), 2008);

Total energy = Decreasing energy consumption + Energy generation;

Gain energy = (tot energy of PDS or tot energy 1DS – tot energy of CF) × 100 / tot energy of CF

CHAPTER 9

General Conclusions and Recommendations

On doing a retrospective analysis of the work accomplished in this thesis, a number of issues come forth. Concluding remarks have been discussed throughout the document for the particular issues addressed. The overall conclusions are outlined in this chapter. The contributions of the approach followed in this thesis will be highlighted as a summary list

1. To investigate difference in effects between periodic and one-time application of digested slurry (PDS and 1DS, respectively) to wet rice fields by a slurry irrigation system using controlled pot cultivation and actual wet rice field tests. Fertilizer application rates were 120 kgN/ha for PDS and 220 kgN/ha for 1DS. Both experiments gave similar results for growth duration and nitrogen (N) use efficiency. During the tillering stage, plants after PDS had lower stem number and SPAD values (chlorophyll content of leaves) than plants after 1DS, but the values increased during the panicle initial stage and were higher than 1DS during the ripening stage. PDS exhibited significantly higher levels of N uptake, agronomic efficiency, and fertilizer N recovery efficiency than 1DS. However, improving operation of periodically supplied digested slurry on paddy fields for achieving optimal conditions and test with other varieties in the same conditions still be essential.
2. From the first study, to use digested slurry will be achieved a huge amount of rice straw. Therefore, for using rice straw long time, storage will be crucial to keep qualities of rice straw. The study of basic properties and quality changes during storage on rice straw would be conducted. All of storage conditions affected

rather on qualities of rice straw. Storage time and temperature increased, qualities would be decrease. Especially, temperature at 30°C affected more than other and duration time was stopped on 4 months in the first harvest year. Furthermore, high effects were on the first month for storage time in both harvest years, after that, there was a bit difference. Further, the wide varieties of rice straw will be studied for being collecting characteristics of rice straw, moreover the other characteristics will be investigated as well.

3. For development of a calorimetric method by using thermodynamically open system to estimate energy content of biomass solid fuel. Mass and energy balances were accompanied. Therefore, amount of sample weight was the important factor affecting energy output of OSC and achieved the best result at using around 0.2 g of sample weight. Furthermore, estimation of other energy outputs (the unaccounted) which was a high value of energy output was examined from the calibrated known, was not an individual value in each examination which may be affected less or more to the simple calorimeter accuracy.
4. Uncertainty of OSC had quite low with ± 1.74% multiplied by a coverage factor was 2 and providing a level of confidence of approximately 95%. In addition, the model had ability to predict *HHV* at $P < 0.05$ and standard error of estimate was ± 0.183. This model using OSC as an instrument to estimate the heating value by measure 3 main parameters; combustion output, gained heat and other output. However estimating heating value by OSC, combustion system and ignition time should be improving and if the model is derived from gained heat merely, it will be convenient measuring.

5. Relationships by linear multiple regression analysis between major constituents (carbon, nitrogen, moisture, and ash concentrations) and the higher heating values of rice straw were developed, as $HHV = 11713.62 + 74.34C + 3571.04N$ and between storage conditions (storage period and temperature) and the higher heating values as, $HHV = 17007.89 - 9.17t + 0.05T$ where, C and N are carbon and nitrogen concentrations (%db), t is storage period (day) and T is storage temperature (°C). These equations can estimate *HHV* of straw around 35.58%db to 42.68%db of *C*, 0.37%db to 0.67%db of *N*, after harvest until 4 months for storage period, and 10 to 30°C of storage temperature. The new equations were well results with high coefficient of determination, and small bias errors, with the 95% confidence level. Therefore these equations are acceptable for estimations the heating value of rice straw. Nevertheless, the wide varieties of rice straw and wide moisture content will be studied in the future.
6. From study influence of storage conditions on rice straw fast pyrolysis, pyrolysis stage of rice straw was separated to four stages by TG and DSC curves, consist drying, heating, degradation and heating and aggregation of char. The rice straw had highest amount of heat to raise the temperature based on a specific dry weight in the degradation stage of pyrolysis process. Degradation stage was an important stage, in which highest heat flow rate and highest specific heat occurred. Specific heat (C_p) of rice straw with temperature lower than 120°C is a constant value with 1.30 kJ/kg °C. The specific heat (C_p) before degradation stage is available and given by $C_p=4.2715 - 0.0396T + 0.0001T^2$, where T is temperature between 120°C to 250°C. Ideal pyrolysis temperature range for bio-gas production would completely finish around 470°C to 500ºC. Storage conditions related to residual

mass loss and heat requirement. In all of long storage time condition, residual mass loss became smaller, but higher heat requirement than initial condition. Heat requirement to increase the temperature of 1 kg of rice straw from room temperature to 600°C, for initial rice straw was 862 kJ. For storage temperature after stored 4 months, minimum and maximum heat requirements occurred at 20°C and ambient temperature, respectively. Furthermore, cut straw were the lowest of residual mass loss and heat requirement with 963 kJ/kg were required to increase the temperature from room temperature to 600°C.

However, the application of digested slurry as a liquid fertilizer requires further study, including transporting the fertilizer to rice fields, controlling the amount of N and providing a uniform spread. The results from this study are useful for use rice straw as renewable energy which can predict behavior of rice straw in pyrolysis process. However, several assumptions and considerations still require attention and they are worth mentioning in subsection so as to encourage future research. The applicability of the thermal decomposition of other varieties, the analysis of conditions commonly applied in laboratory scale or commercial pyrolysis processes such as heating conditions, particle size, feed rate, condensing conditions, etc. have been out of the scope of this study are still waiting for investigate and discussion in the future. Besides, the observation of pyrolysis products by using gas chromatography-mass spectrometry could have provided even more insight into the study.

One of the most important cognizances of this work lays in the green energy cycle results. From the results, digested slurry by methane fermentation can apply to rice fields as well as fertilizer. That is, energy consumption for producing chemical fertilizer

will decrease. Furthermore, by-product from rice fields (rice straw) can convert to fuel as pyrolysis oil, that is, energy generation will achieve. Therefore, using rice straw which was produced from using digested slurry as fertilizer to be a material for pyrolysis is a wishing way to recycle food waste and agriculture waste to produce green energy.

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